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THE CHEMISTRY

OF THE

COAL-TAR DYES

BY

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SECOND EDITION, REVISED AND ENLARGED

NEW YORK

D. VAN NOSTRAND COMPANY

25 PARK PLACE

1919

UNIV. OF
CALIFORNIA

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PREFACE TO THE SECOND EDITION

THE exhaustion of the first edition and the continued steady demand having made necessary the publication of a new edition, the author has taken advantage of the opportunity to revise the entire volume and make such additions as recent advances in the dye industry warrant. Errors in the minutiæ of formulas and reactions have been sought for and corrected. Advantage has also been taken of the suggestions of many in whose hands the volume has found a friendly reception.

Two chapters have been added upon the subjects: Vat Dyes and Thiazol Dyes. The Vat Dyes from their fastness to all deteriorating influences have prior claim upon the attention of dyers to-day. Though difficult of manufacture, good progress has already been made toward their production in this country.

Among sources consulted in the preparation of this edition may be mentioned "Manufacture of Intermediate Products for Dyes," by John C. Cain; Dr. Wahl's "L'Industrie des matières colorantes organiques," translated by Atack; "Organic Coloring Matters," by Green; and "The Chemistry of Dyestuffs," by Fort and Lloyd.

Should the present edition meet with as favorable a reception as was accorded to the first, it will appear that some definite service has been rendered to students of the subject in this critical period of our Coal Tar Dye Industry.

IRVING W. FAY.

POLYTECHNIC INSTITUTE,
Brooklyn, N. Y., November 1918.

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PREFACE TO THE FIRST EDITION

THIS book is intended for those students and dyers who have a good knowledge of general chemistry, and some knowledge of organic chemistry.

The object is to present, briefly, the origin and history of coal-tar production, and a discussion of the intermediate products between the coal-tar and the dyes themselves.

The methods of making the dyes are taken up, followed by a study of the relations of the great classes of dyes, and also the individual dyes themselves, to one another in the same class. The development of one color from another by a change in its composition is explained, and tables showing the variation of color accompanying change of composition are included. The proof of constitution is in many places given in such detail as to allow the student to comprehend the bases for the structure of the complex molecules of the dyes.

The significance of the chromophors and chromogens in the different classes of dyes is discussed. The use of mordants and the character of the union between the dyes and animal and vegetable fibres are also included.

A few manufacturing processes are introduced here and there in detail, to give clear conceptions of this phase of the subject. Some practical experience to assist in comprehending the theory of the subject is made possible by a course of experiments, the performance of which aids in vivifying this difficult and interesting subject. It is hoped that this feature of the work will produce a more tangible result than could otherwise be possible.

The terms sulphonic acid and sulpho acid are used inter-

changeably in indicating those compounds containing the SO_3H group. The author wishes to acknowledge the kindly and helpful suggestions received from Dr. Arthur C. Langmuir, Professor John C. Olsen, and Dr. Bernard C. Hesse, in the preparation of this volume.

Among the many sources drawn upon may be mentioned: Chemie der organischen Farbstoffe von Dr. R. Nietzski; Tabellarische, Uebersicht der künstlichen organischen Farbstoffe von Schultz uud Julius, also Arthur Green's translation of the same; A Dictionary of Dyes and Mordants, by Rawson, Gardner and Laycock; Cain and Thorpe's Synthelic Dyestuffs and Intermediate Products; Chemistry of Dyestuffs by Georgievics. Practical Methods of Organic Chemistry by Gattermann. Organic Chemistry by Bernthsen; Organic Chemistry by Richter; and Cain's Chemistry of the Diazo Compounds.

IRVING W. FAY.

BROOKLYN, N. Y., December, 1910.

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COAL-TAR DYES

CHAPTER I

INTRODUCTION

Origin of the Coal-tar Dyes

The discovery of the first coal-tar dye was the result of an accident; one of those happy accidents without which many of the strides of chemical science could never have been taken. If an unusually alert mind had not been making the observations this accident would have passed unrecognized and the opening of a new department of the science postponed for no one knows how many years.

In 1856 a young English chemist, W. H. Perkin, was working as an assistant to the celebrated German chemist A. W. Hoffman, who at that time held a position in London. As the Easter vacation of that year approached Hoffman planned to be away from the laboratory for the holiday. This leisure time afforded young Perkin opportunity to try some experiments which had greatly aroused his interest. He wished to produce synthetically no less a substance than the valuable alkaloid quinine.

For this purpose he brought together a nitrogenous substance known as allyl-toluidine, bichromate of potash, and strong sulphuric acid. The attempt was a failure so far as obtaining quinine or anything like it, but he noticed that a colored product had been formed. The most interesting feature of this work was the quick perception of some possible value for the new substance. Few chemists would have

pondered the result, or in the disappointment of the moment have paid any attention to the unexpected product.

On the contrary, it aroused the curiosity of Perkin to such a degree that he resolved to investigate the peculiarity of this strange reaction by using simpler substances. He then employed in place of allyl-toluidine, the simpler body known as aniline. This was treated with bichromate of potash and sulphuric acid. An unpromising black residue was the only result. Extraction with alcohol however dissolved out a lilac coloring matter which was later to become the first commercially successful coal-tar dye.

During the preliminary stages of its purification, Hoffman returned from his vacation and Perkin showed him the new dyestuff. As it was not crystalline, and as Hoffman had a horror of substances that would not crystallize because of the difficulty in obtaining them in a state of purity, he advised Perkin to throw it away and have nothing to do with it. Perkin's interest was, however, by this time too thoroughly aroused to give it up.

The dye was finally purified and given the name of mauve, by which it became familiar in England. Upon the continent it was known as aniline violet or Perkin's violet. It is now more often called mauveine.

The dye appeared upon the market in the form of an alcoholic solution. It was too expensive save for the dyeing of silk for which it was greatly prized by the manufacturers. At the present time it is used only to a slight extent in the form of a sulphate called rosolan for bluing white silk and for printing the English penny postage stamps. (This use ceased at the end of the last reign.) In this way England maintained for half a century a unique memorial to her celebrated chemist, perpetuated even in the remotest corner of the world wherever its mail service may have penetrated.

Though the mauve never attained a very high degree of practical importance, none was ever of so much value in exciting research for the discovery of other dyes.

Perkin's keen observation and his persistence in developing his new dyestuff were rewarded both with commercial

success and with imperishable fame in the scientific world. He had the rare good fortune to witness for fifty years the cultivation of this entirely new field of dyestuff chemistry, wherein the most magnificent scientific results have been attained and enormous industrial fruits have been reaped by the utilization of one of the most worthless by-products in the technical world.

The processes of manufacture were in the early years of the industry necessarily crude and the products impure. Nevertheless by these very empirical methods great progress was made, and research was stimulated to an unwonted degree.

In the year 1865, the theoretical side of the science was enriched by the conception of August Kekulé that the molecule of benzene had the form of a six-sided ring or hexagon with a single hydrogen attached to each carbon atom. This extremely important and fruitful idea has given its author imperishable fame.

From this time, the advances became gradually more scientific and research could proceed on rational lines. The chemical activity stimulated by repeated and brilliant successes in the coal-tar dyes was not wholly confined to this field, but invaded the domain of the natural colors. Four years after this, the discovery by Graebe and Liebermann of the constitution of alizarine, the color principle of the madder root, used from time immemorial for dyeing the famous Turkey-red, showed the fruit of the increasingly scientific character of investigation. This discovery drove the culture of the madder root out of Europe and replaced it with a superior product made from the derivatives of coal-tar.

Twenty years later, 65 tons of a 10 per cent alizarine paste were produced in Europe each day. With the long continued manufacture, the price fell from $1.60 per pound in 1870 for a 10 per cent paste to 20 cents per pound in 1900 for a 20 per cent paste.

A similar fate is about to overtake the cultivation of indigo in its stronghold in the fields of India. Since the

oxidation by Nencki in 1874 of indol to indigo-blue by the use of ozone, unremitting studies to find its constitution have been carried on. Adolph Baeyer and his students and many others have brought out various successful methods of making indigo from derivatives of coal-tar, some of which are successful commercial rivals of the natural product. To such a degree have the synthetical methods progressed that one German firm in 1900 manufactured as much indigo of a quality superior to the Indian product as could be grown upon a quarter of a million acres of ground.

Following the discovery of rosaniline in 1859, dyes of a great variety of shades were obtained and often of such extraordinary beauty as to command fabulous prices. In 1874 the magnificent dye, eosin, discovered by Heinrich Caro, sold for $100 per pound, and on account of its brilliant dyeings upon silk, it found a demand even at that high price.

In 1900, the combined production of benzene and toluene amounted to between 25,000 and 30,000 tons. As these form about one per cent of the crude tar, it follows that 3,000,000 tons were subjected to distillation to obtain these products.

From the early manufacture, of a nature so crude that during suits, in Paris in the early days, of one manufacturer against another for infringements of patents neither counsel nor experts could either dispute or establish the identity of products made by different oxidizing agents upon the same raw materials, to the present day, when research is often able to reveal the actual structure and how the complex dye molecule is built up, is a long history of processes which have been improved by a most persistent and thorough study, both theoretical and practical, by the celebrated investigators of the scientific world.

CHAPTER II

COAL-TAR AND ITS PRODUCTS

When bituminous coal is thoroughly ignited in stoves and furnaces and a draught of air freely circulates through the mass, three principal products are formed: one is water vapor, a second carbon dioxide, and a third the ash.

If coal be heated equally hot, but inside a long cast-iron or earthen retort shut off from all contact with the oxygen of the air, then a great number of products is formed wholly unlike those resulting from ordinary combustion. This operation is known as destructive distillation and has been carried on to an enormous extent in all civilized countries for the production of illuminating gas.

An estimate made twenty years ago placed the amount of capital invested in gas works in England alone at $35,000,000.

Four chief products result from the destructive distillation of bituminous coal as carried on in the gas works: coal-gas, ammoniacal liquor, coal-tar, and coke. The coal-tar, once a great nuisance in the gas industry, is the only substance obtained from the coal which is of importance to the dye industry. It contains more compounds than the other three products combined.

In the distillation of coal, the tar leaves the hot retort as a heavy vapor and condenses in the water of the hydraulic main and in the scrubbers, while the illuminating gas passes on through another train of purifying apparatus.

The tar itself is a deep black, opaque, syrupy liquid of unpleasant odor, a little heavier than water and having an average specific gravity of 1.08 to 1.20. Its black color is due to finely divided free carbon which varies greatly in the tar from different works, ranging from 7 to 33 per cent.

Crude coal-tar is used to some extent for making "tar-paper," for preserving timber, and coal-tar pitch as a protective paint for acid pipes and condensing vessels, and further as a cement in forming certain furnace linings.

The constituents of tar may, according to their chemical reactions, be divided into three classes: first, the hydrocarbons, second, the phenols, third, the nitrogenous compounds.

The hydrocarbons as the name suggests are composed of carbon and hydrogen. They are chemically indifferent substances exhibiting neither acid nor alkaline properties. They form at the same time the principal and most valuable portion of coal-tar. Benzene, toluene, xylene, naphthalene, and anthracene are the most important of these hydrocarbons.

The second class comprises oxygenated bodies called phenols; they consist of carbon, hydrogen and oxygen. They are weakly acid bodies and collectively are known as the "tar acids." They consequently dissolve in a solution of the caustic alkalies while they are insoluble in dilute acids. Carbolic acid or phenol and cresol are the most important of these bodies.

The third class is made up of bodies composed of carbon, hydrogen, and nitrogen. These are of a basic nature and dissolve in acids. A large number of individual substances is comprised in this class, but none in sufficiently large amount to render profitable its technical preparation from this source.

There remain a number of other substances among which are sulphur, oxygen, and nitrogen derivatives of the hydrocarbons, and carbon disulphide, but these are not isolated, and occur chiefly as impurities in the other classes and serve to make more tedious their ultimate purification.

The increasing employment of the O. W. Hoffman ovens for producing coke, wherein the volatile constituents of the coal are saved, augments the total annual product for the world which at present cannot be far from 3,000,000 tons. A large part of this is distilled for its various products.

The Distillation of Coal-Tar

The separation of the constituents of coal-tar depends upon the selective results of fractional distillation. This process is based upon the fact that when a mixture of two substances having different boiling-points is heated, the one having the lower boiling-point will be most easily converted into vapor and escaping from the retort pass most rapidly over into the distillate. After the greater part of the lower boiling liquid has passed over, then boiling ceases for a time until the temperature rises nearly to the boiling point of the second constituent when the boiling recommences and the vapor passing over is condensed and collected in a second receiver.

In practice, if a mixture of absolute alcohol which boils at 78.3° C. and water boiling at 100° C. were distilled, almost pure alcohol would pass over first, then a mixture of alcohol and water, and finally almost pure water. Approximately complete separation of the mixture would require repeated distillation. A Savalle still in the case of alcohol will yield an almost pure alcohol in one or two operations.

The boiling points of the substances in coal-tar vary widely: benzene boils at 80° C. and anthracene at 370° C. It is therefore feasible by separating the different fractions, to separate the constituents effectually. The first fraction will contain different compounds from those in the second; the second different from those in the third, and so on.

The process of distillation is carried on in enormous vertical cylindrical retorts often capable of containing 35 tons of tar for a single operation. The bottom of the still is concave upward, allowing the heat to penetrate the mass of tar and protected from direct flames by a curtain or arch of bricks. This prevents the overheating of the residuum and the burning on of a layer of coke upon the bottom of the still. The still is entirely enclosed in brick walls to prevent radiation and to form passages so that flames may pass around and half way up the vertical height of the still before escaping to the flue.

The capital or head of the still has an outlet pipe 12 inches in diameter diminishing to 6 inches where it joins the condensing worm. The worm may be from 140 to 200 feet long, 4 to 6 inches in diameter, coiled in a tank of water, which is allowed to become warm as the distillation progresses to prevent its clogging with products that are solid at the ordinary temperature. To further prevent clogging a steam pipe enters at the beginning of the worm and the rush of steam melts and pushes onward any products which may have solidified in the worm.

The still is provided with a large inlet pipe, the end of which projects beyond the wall of the still, lest the ammonical liquors of the crude tar in trickling down the hot iron cause serious corrosion. The outlet pipe is at the lowest point of the still, opposite to the fire. A safety valve or a cover held in place by its own weight obviates any danger of explosion and the fire and ash pit are so protected by masonry that in case of an overflow the boiling tar may not be ignited.

A tell-tale pipe gives warning when the still is full and a long stemmed thermometer surrounded by mercury and iron filings in an iron pipe affords control of the temperature of distillation. A circular perforated steam pipe passes around the lowest part of the bottom near the outer wall and during the latter part of the process superheated steam agitates the thick tar and assists in carrying off the heavy vapors. A manhole gives access to the interior of the retort for cleaning.

Experience with thick tars has developed the use of mechanical agitators which stir the heavy tar by the dragging around of chains over the bottom of the still. So successful has this improvement been that a run of fifteen distillations of 25 tons each is recorded without burning on of a layer of coke or need of interruption save as a precaution.

The process of distillation is carried on until a temperature of 400° C. is attained, when about 55 per cent of the original tar remains as a thick black pitch which turns solid on cooling. It is thus necessary to run out the pitch while still warm enough to flow and yet cool enough to be secure

against spontaneous ignition in the air. The pitch is sometimes softened by running in some of the waste oils from a previous distillation.

The distillate is caught in separate receivers and they are changed from time to time as the temperature in the still increases so as to keep the fractions by themselves. Uusually the distillate will be separated in five fractions. These fractions have the following technical names:

First runnings, or "first light oil".to 105° C.
Light oil.....to 210° C.
Carbolic oil.....to 230° C.
Creosote oil.....to 270° C.
Anthracene oil, or "green oil"....270°–400° C.

The temperature at which the distillation is discontinued depends upon whether a soft or hard pitch is desired for the residuum. Sometimes the distillate is caught in three separate portions instead of five; in that case they have the names and ranges of temperature given below:

Light oil.....to 170° C.
Heavy oils.....to 270° C.
Anthracene oil.....to 400° C.

The first distillates from the tar are crude mixtures of various substances and they require agitation with alkalies and acids and several washings with water to remove impurities. Finally they are subjected to repeated fractional distillation to separate the individual substances in a state of purity.

The "first runnings" and "light oils" yield benzene, toluene, and xylene: the "carbolic oils" give phenol, cresol, and naphthalene; and from "anthracene oils" or "green grease" is obtained anthracene.

In the further treatment of the "first runnings" and "light oils" they are first subjected to fractional distillation. A first low boiling portion (containing carbon bisulphide, fatty

acids and acetonitrile) and a last high boiling portion (united afterward with the carbolic oils) are both removed. The middle portion is thoroughly agitated with caustic soda to remove phenols, then with sulphuric acid to eliminate the bases (pyridine, quinoline), hydrocarbons of the acetylene and ethylene series, naphthalene, and thiophene.

This purified middle portion is again distilled to obtain so called "crude benzene." From this product pure benzene, toluene, and xylene are separated from one another by rectification in a special apparatus known as the "Savalle" still.

The carbolic oils on standing deposit solid crystalline naphthalene. This is removed from the liquid portion by centrifugal machines and then pressed. The same oil can be made to yield more naphthalene, after the removal of phenols by caustic soda. The crude naphthalene is freed from adhering phenols by washing with hot caustic soda, and from bases and other impurities by agitation with five to ten per cent concentrated sulphuric acid: it is afterward washed with very dilute alkali and distilled or sublimed.

The separation of the phenols and cresol from the carbolic oils depends upon the fact that they dissolve in caustic soda forming soluble salts. The "carbolic oils" are therefore agitated with dilute caustic soda, and the resulting aqueous alkaline solution drawn off from the oil has steam blown through it to remove small amounts of naphthalene and other hydrocarbons which persist as impurities. Addition of hydrochloric or sulphuric acid decomposes the salts, and precipitates the phenols which, after separation from the liquor, are subjected to fractional distillation. The phenol or carbolic acid thus obtained chemically pure is a white solid melting at 42° C.; the three isomeric cresols form a liquid mixture. None of the higher phenols are separated; but they are used directly for preserving timber.

The last distillate from the coal-tar, the so-called "anthracene oil" or "green grease" is a thick greenish buttery mass which contains about ten per cent of anthracene mixed with a large number of other substances which have so far been

found of little value. The processes of purification whereby the percentage of anthracene rises to 25 to 40 per cent, then 50 to 60, then to 80 per cent, and finally to chemical purity, are explained later under the head of anthracene.

The Constituents of Coal-Tar

A large number of compounds have been isolated from coal-tar and their melting and boiling points ascertained and their general character more or less investigated. They fall naturally into four different classes: hydrocarbons, other neutral bodies, bases, and phenols or acids. Of these but few are separated and employed in dye manufacture; by far the larger proportion are used as mixtures for various industrial purposes.

CONSTITUENTS OF COAL-TAR

1. Hydrocarbons

	Formula.	Melting-point.	Boiling-point.
Crotonylene	C_4H_6	Fluid	20° C.
Hydrocarbons (ethylene series)	C_nH_{2n}	.....	.....
Hydrocarbons (methane series)	C_nH_{2n+2}	.....	.....
Benzene	C_6H_6	6° C.	80.4° C.
Toluene	C_7H_8	Fluid	110.3° C.
o-xylene	C_8H_{10}	−28° C.	142° C.
m-xylene	C_8H_{10}	−54° C.	139° C.
p-xylene	C_8H_{10}	15° C.	138° C.
Styrene	C_8H_8	Fluid	146° C.
Mesitylene	C_9H_{12}	"	163° C.
Pseudocumene	C_9H_{12}	"	166° C.
Naphthalene	$C_{10}H_8$	79° C.	218° C.
Methylnaphthalene	$C_{11}H_{10}$	*a* −20°, *b* 33° C.	242° C.
Diphenyl	$C_{12}H_{10}$	71° C.	254° C.
Acenaphthene	$C_{12}H_{10}$	95° C.	277° C.
Fluorene	$C_{13}H_{10}$	113° C.	295° C.
Phenanthrene	$C_{14}H_{10}$	99° C.	340° C.
Fluoranthrene	$C_{15}H_{10}$	110° C.	above 360° C.
Anthracene	$C_{14}H_{10}$	213° C.	351° C.
Methylanthracene	$C_{15}H_{12}$	190° C.	above 360° C.

	Formula.	Melting-point.	Boiling-point.
Pryene	$C_{16}H_{10}$	149° C.	260°(60mm.)C.
Chrysene	$C_{18}H_{12}$	250° C.	448° C.(?)
Picene	$C_{22}H_{14}$	364° C.	520° C.

2. Other Neutral Bodies

Carbon disulphide	CS_2	Fluid	47° C.
Ethyl alcohol	C_2H_5OH	−130° C. (?)	78.3° C.
Acetonitril	C_2H_3N	−41° C.	81.6° C.
Thiophene	C_4H_4S	Fluid	84° C.
Thiotolene	C_5H_6S	"	113° C.
Thioxene	C_6H_8S	"	134° C.
Benzonitrile	C_7H_5N	"	191° C.
Phenylthio carbimide	C_7H_5NS	"	220° C.
Carbazole	$C_{12}H_9N$	238° C.	351° C.
Phenylnaphthyl carbazole	$C_{16}H_{11}N$	330° C.	above 440° C.
Coumarone	C_8H_6O	Fluid	169° C.

3. Bases

Pyridine	C_5H_5N	Fluid	114.8° C.
Pyrrol	C_4H_5N	"	131° C.
Picoline	C_6H_7N	"	130° C.
Lutidine	C_7H_9N	"	157° C.
Collidine	$C_8H_{11}N$	"	171–172° C.
Aniline	C_6H_7N	−8°	184° C.
Quinoline	C_9H_7N	"	239° C.
Quinaldine	$C_{10}H_9N$	"	247° C.
Acridine	$C_{13}H_9N$	110° C.	above 360° C.

4. Phenols

Phenol	C_6H_6O	43° C.	183° C.
o-cresol	C_7H_8O	31° C.	188° C.
p-cresol	C_7H_8O	36° C.	198° C.
m-cresol	C_7H_8O	4° C.	201° C.
a-naphthol	$C_{10}H_8O$	95° C.	278–280 °C.
b-naphthol	$C_{10}H_8O$	122° C.	286° C.
Xylenols and other high boiling phenols			

CHAPTER III

THE HYDROCARBONS AND THEIR DERIVATIVES

Benzene C_6H_6 is, when pure, a clear colorless liquid of characteristic penetrating ethereal odor. It is very inflammable and burns with a smoky flame, which sends up black clouds of unconsumed carbon.

The soot rising from the flame is accounted for by the large percentage of carbon present which is not supplied with sufficient proportion of oxygen from ordinary air for its complete combustion. Benzene boils at 80.4°; below 5.4° it is solid.

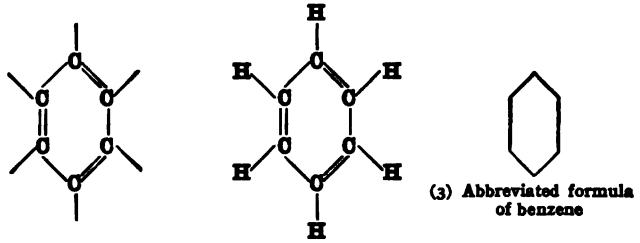
The illuminating power of coal-gas is partly due to benzene, and it was first discovered in London illuminating gas and not in coal-tar from which it is now largely obtained.

A London company in 1815 was engaged in manufacturing illuminating gas and sending it out to their patrons compressed in cylinders. In these cylinders an oily liquid condensed, and the company submitted some of it to Faraday for examination. He happened just then to be at work upon the compressibility of gases. The result of his investigation showed that the new liquid consisted of but two elementary substances: carbon and hydrogen. The former was present to the extent of 36 parts and the latter 3 parts by weight.

Faraday called the new body bicarburet of hydrogen and gave it the empirical formula C_2H_2, which at the present time would be written C_6H_6. The same oil was obtained later from different sources; but it was not until twenty years afterward, in 1845, that it was discovered by Hoffman in coal-tar.

Twenty years more elapsed before an explanation of its structure, as written in every text to-day, was attempted.

In 1865 Kekulé proposed a formula for benzene which has survived more than a generation of criticism. This formula exhibited the positions and relations of the six carbon and six hydrogen atoms in the molecule of benzene C_6H_6. According to Kekulé, each of the six carbon atoms is attached by two valences to its neighbor on one side, and by one valence to the neighbor on the other side. A glance at the following formula will make this clear.



(1) Benzene ring (2) Benzene (3) Abbreviated formula of benzene

The six free valences of the ring, one upon each carbon atom, serve as the points of attachment of the six hydrogen atoms, and the complete formula of benzene is shown in Fig. 2.

Benzene is one of the most stable compounds; attempts to break up this ring and force a decomposition of the molecule requires the most powerful oxidizing agents. Yet, while the six carbon atoms of the benzene ring are so difficult to separate from each other, the six hydrogen atoms are less firmly attached to the carbon atoms themselves and they are with comparative ease replaceable by simple elementary atoms: chlorine, bromine, etc., or groups of elements —the nitro group ($-NO_2$) or the amino group ($-NH_2$), etc.

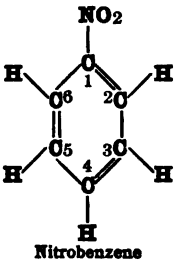
A formula which thus exhibits the relative positions of atoms in a molecule, as in the benzene molecule above, is called a constitutional or structural formula. Other constitutional formulas have been proposed by Claus, Ladenburg, Armstrong, and Baeyer to account for some of the properties of benzene; but none have attained the consideration given to the Kekulé hexagonal or ring formula.

Mono-derivatives of Benzene

Nitrobenzene.—Of all the reactions into which benzene enters, that with strong nitric acid leads in importance. A single molecule of nitric acid acting upon a molecule of benzene forms, according to the following reaction, a new substance, nitrobenzene and water:

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O.$$

There is only one product known as nitrobenzene, no matter how the experiment may be carried out. This seems to show that by the replacement of any one of the six hydrogens of benzene the result would be one and the same product. By a mass of other evidence, it has been proved that all the six hydrogens are of equal value and that the replacement of any one of the six would produce the substance represented by the formula,



Nitrobenzene

For convenience of reference, the carbon atoms have been numbered as shown in the formula for nitrobenzene.

With other groups or elements replacing a single hydrogen of benzene, the same rule holds that, e.g., only one monochlorbenzene or one monobrombenzene is possible or has ever been discovered. Nitrobenzene is a pale yellow liquid heavier than water which turns solid in the cold and melts at 3°. It possesses an intense odor of bitter almonds.

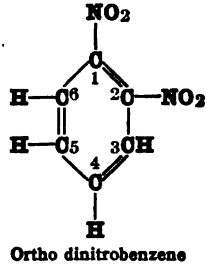
Diderivatives of Benzene

Dinitrobenzenes.—If fuming nitric acid be allowed to act upon benzene, then two hydrogen atoms are replaced by

two nitro groups giving rise to dinitrobenzene of the empirical formula $C_6H_4(NO_2)_2$. Not one, only, but three dinitrobenzenes are formed, and all possess the same empirical formula.

If we examine Kekulé's formula for benzene, we may understand why there are three and no more.

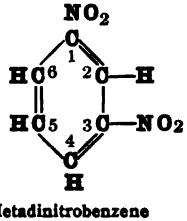
In the following formula,



Ortho dinitrobenzene

if we suppose one nitro group to replace the hydrogen atom at 1 and a second hydrogen at 2 we shall have what is called orthodinitrobenzene. The nitro groups are upon neighboring carbon atoms, and, if the groups were in the position 2 and 3, or 3 and 4, or 4 and 5, or 5 and 6, or 6 and 1, they would still be attached to neighboring carbon atoms and they would still form one and the same orthodinitrobenzene.

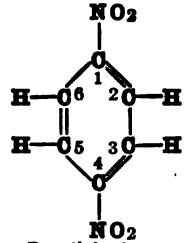
If the nitro groups replace the hydrogens in position 1 and 3, or 2 and 4, or 4 and 6, etc., then the resulting compound is known as metadinitrobenzene, represented in the following formula:



Metadinitrobenzene

Lastly, when the substituting nitro groups take positions 1 and 4, or 2 and 5, or any other positions which are opposite

to each other, the resulting product is paradinitrobenzene as shown below:

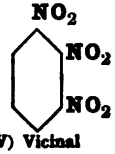


Paradinitrobenzene

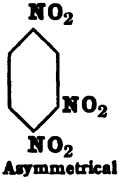
Substances like the dinitrobenzenes which have the same empirical formula but a different constitution, are called *Isomers*, and they are said to be *Isomeric* with one another. The same atoms and the same number of each kind are present in all three. Differences of structure alone account for their being different substances. The *o*- and *m*-compounds are colorless, while the *m*-compound is pale yellow. All are crystalline solids. What has been said in reference to the number and structure of the dinitrobenzenes applies with equal force to all diderivatives of benzene, e.g., dichlorbenzenes, or dibrombenzenes or dimethylbenzenes, etc.

Triderivatives of Benzene

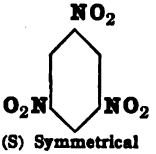
If three hydrogens of the benzene ring are replaced by three nitro-groups, then, too, there are three triderivatives, or three trinitrobenzenes. They are represented as follows:



(V) Vicinal



(A) Asymmetrical



(S) Symmetrical

Here then, are three isomeric triderivatives of benzene.

If the three groups are unlike, then a larger number of isomers is possible. With the substituting groups all alike, there are three tetra, one penta, and one hexa derivative of benzene.

Toluene, $C_6H_5CH_3$, is so named from tolu balsam, whence it was obtained by dry distillation. Commercial toluene is obtained from coal-tar. It may be regarded as benzene in which one hydrogen atom has been replaced by the methyl group $-CH_3$. Indeed, this methyl group may be placed synthetically in the benzene ring by the following reaction:

$$\underset{\text{Benzene bromide}}{C_6H_5Br} + CH_3I + 2Na = \underset{\text{Toluene}}{C_6H_5CH_3} + NaBr + NaI.$$

Toluene may therefore rightly be called methylbenzene or phenylmethane. It is a colorless mobile liquid boiling at 110° and it remains liquid at −20°. At 15° it has a specific gravity of .870. Toluene is very susceptible to the action of a large number of reagents forming many important substitution products which will be studied later.

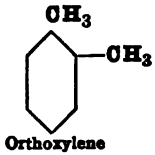
Only one toluene or methylbenzene is theoretically possible or has ever been discovered.

Oxidizing agents attack toluene in a peculiar and interesting way. The ring portion of the molecule remains intact, the methyl group alone undergoing oxidation as shown by the reaction:

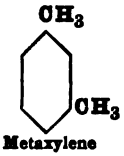
$$\underset{\text{Toluene}}{C_6H_5CH_3} + 3O = \underset{\text{Benzoic acid}}{C_6H_5CO\cdot OH} + H_2O.$$

The oxidation product is benzoic acid, a carboxyl derivative of benzene.

Xylenes, $C_6H_4(CH_3)_2$. When two hydrogen atoms in the benzene ring are replaced by methyl groups, the xylenes are formed. Of these, three are possible and all are known. The three isomeric xylenes have the same formula, $C_6H_3(CH_3)_3$; but they are distinguished from one another by the positions which the two methyl groups occupy in the ring, as shown in the following structural formulas:



Orthoxylene



Metaxylene

Paraxylene

That portion of the light oil from coal-tar which boils at 140° contains a mixture of the three xylenes, but the meta-xylene is present in the largest amount. They all have nearly the same boiling point, so they cannot be separated from each other by fractional distillation. An interesting and indirect method of overcoming this difficulty consists in boiling commercial xylene; with dilute nitric acid when the ortho- and paraxylene become oxidized to the corresponding xylilic acids, the metaxylene remains unacted upon. By treating the mixture with caustic soda, the acids are removed in the form of their sodium salts, and the meta-xylene is obtained pure.

Pure paraxylene may be obtained according to Levinstein when the commercial xylene is distilled with steam. The crystals of paraxylene which separate on cooling the first portion of the distillate are pressed and redistilled.

By Jacobsen's method, all three isomers may be separated from xylene by shaking with strong sulphuric acid. The paraxylene is not affected; but the ortho- and metaxylene are converted into their sulphonic acids: the sulphonic acids are then changed into their sodium salts and these are separated from each other by crystallization.

Distillation of the salts with ammonium chloride regenerates the hydrocarbons.

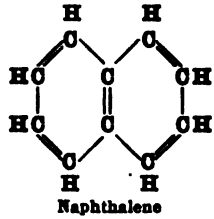
Orthoxylene forms a colorless liquid boiling at 142°. It constitutes from 2 to 15 per cent of commercial xylene.

Metaxylene boils at 139°. It is a colorless liquid having a specific gravity of .8868 at 15° and is present from 70 to 87 per cent in commercial xylene.

Paraxylene is present from 3 to 10 per cent in commercial xylene. It is a colorless liquid which crystallizes at 15° and boils at 138°. From 3 to 10 per cent of paraffine hydrocarbons are also present in ordinary xylene. Formerly, use was made of it as a solvent by the name of "solvent naptha"; but the manufacture of the azo-dyes requires large quantities of it to be converted into xylidine and cumidine.

Naphthalene, $C_{10}H_8$. The structure of naphthalene has been proved to consist of two benzene rings attached to

each other, so that two neighboring carbon atoms are common to the two united rings, as shown in the following structural formula:

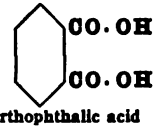


Naphthalene

Abbreviated formula of naphthalene

The proof that this is the structure of naphthalene depends upon a careful study of the reactions which are capable of producing naphthalene from other substances and also of those in which naphthalene is decomposed, forming other new substances. The line of proof is of such interest and clearness and so conclusive that it will be stated in detail.

First by energetic oxidation of naphthalene, phthalic acid is obtained—this is a benzenedicarboxylic acid; the two carboxyl groups are further known to be attached to carbon atoms in the benzene ring which are in neighboring positions. This shows clearly that one benzene ring at least is contained in the molecule of naphthalene, as shown in the following structural formula:



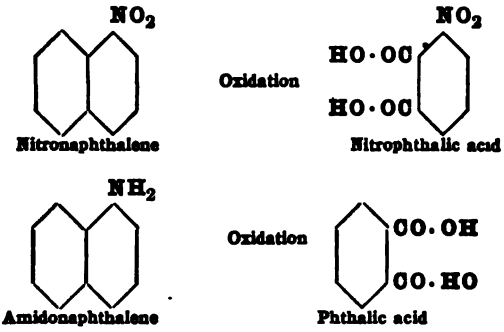
Orthophthalic acid

How may it be further shown to contain a second benzene ring? By allowing nitric acid to act upon naphthalene; one nitro group replaces a hydrogen atom of naphthalene and forms nitronaphthalene.

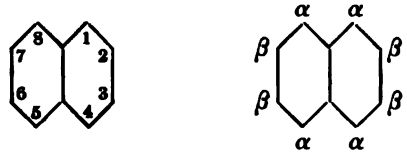
By oxidation of this nitronaphthalene nitrophthalic acid is formed. This fact alone is of little assistance, unless it is coupled with the following, viz., if nitronaphthalene is reduced, the nitro group loses oxygen, gains hydrogen and aminonaphthalene results. Now an interesting difference

from nitronaphthalene is shown when aminonaphthalene is oxidized; for oxidation produces simply phthalic acid in place of nitrophthalic acid. Does this not show that the portion of the molecule containing the nitro group was in the form of a benzene ring?

In the second oxidation the nitro group converted to amino-group was destroyed, yet producing phthalic acid, leaving us to draw but one conclusion, that the other part of the molecule not containing the nitro or the amino group also had the form of a benzene ring. The following indicated reactions will clarify these ideas:



For convenience in designating the derivatives of naphthalene the carbon atoms are either numbered or lettered as shown in the following diagram.

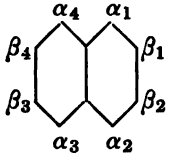


All four of the positions lettered α or 1, 4, 5, 8, are of equal value when any one of these four hydrogens is replaced by a substituting group. Likewise the four positions lettered β or 2, 3, 4, 6, 7, are of equal value in a similar manner. Two monoderivatives are therefore possible in naphthalene instead of one as in benzene.

If an —OH group enter any one of the α positions, or each

one in turn, only one substance α-naphthol will result, and if any β position is occupied then β-naphthol is formed and nothing else. This method of designation is sufficient for mono-derivatives of naphthalene, but not when there are two substituting atoms or groups of atoms.

When both substituting groups are present in the molecule, it becomes necessary to distinguish the letters from one another, and this is done by numbering the letters as shown in the diagram below.

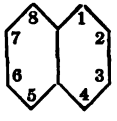


If two chlorine atoms, for example, in dichlornaphthalene, are in the same ring, then the two letters are joined by a single line: orthodichlornaphthalene $C_{10}H_6Cl_2(\alpha_1—\beta_1)$; the metadichlornaphthalene $C_{10}H_6Cl_2(\alpha_1—\beta_2)$ and paradichlornaphthalene $C_{10}H_6Cl_2(\alpha_1—\alpha_2)$.

If the two chlorine atoms are in different rings, then the letters are joined by a double line $C_{10}H_6Cl_2$ $(\alpha=\alpha)$ or $(\alpha=\beta)$, etc.

The possible number of substitution derivatives, of naphthalene, when the atoms or groups are all alike, will be two monoderivatives, ten biderivatives and fourteen triderivatives. When the substituting groups are different, the number of isomers is much larger.

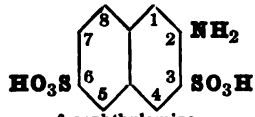
For representation of the structure of the more complex derivatives of naphthalene, numbers alone are also often used to show the exact position of the substituting groups, as in the following diagram:



For example β-naphthylamine disulphonic acid

$$C_{10}H_5(NH_2)(SO_3H)_2\ 2:3:6$$

is easily distinguished if it be borne in mind that the numbers are in the same consecutive order as the substituting groups which are enclosed in the parentheses, then the above compound would have the following structure:



β-naphthylamine disulphonic acid 2:3:6

Naphthalene was discovered in coal-tar by Garden in 1820, but its great importance did not appear until the introduction of the azo dyes. It is contained in that part of coal-tar which on distillation passes over between 180 and 200°. The purification consists in crystallization, pressing, washing with caustic soda and sulphuric acid solutions and distilling.

Naphthalene forms lustrous white monclinic plates. The crystals melt at 79.2° and the liquid boils at 216.6°. The odor is pleasant and suggests coal-tar. It is volatile with water vapor and it sublimes easily. A familiar form is " moth balls " for domestic use. Large quantities of naphthalene are consumed in the manufacture of the oxyazo dyes. and of late for the synthesis of indigo.

Anthracene, $C_{14}H_{10}$, is obtained from coal-tar and it is prepared in large quantity from those portions which pass over between 340 and 360°. It is much more difficult to purify than naphthalene. The first distillate called anthracene oil or " green oil " contains but 10 per cent of anthracene, the remainder being made up of other solid hydrocarbons, such as paraffine, phenanthrene, carbazol and chrysene together with liquid oils of high boiling-points. By cooling, the solid matter crystallizes and is separated from the liquid portion by the filter press or centrifugal machine. The crystalline mass is pressed in canvas bags in a hydraulic press at a temperature of 40°. The crude product from the press contains 30 per cent anthracene. It is pulverized and washed free of the light oils by creosote oil or solvent naphtha. It is

then pressed again. This washing dissolves many contaminating substances but fails to remove carbazol.

These washings leave behind a diminished product in which the anthracene has risen to 50 per cent. In this condition it is sold to the alizarine manufacturer.

To purify it further, it is washed with a caustic potash solution to take out the carbazol and then sublimed in an atmosphere of superheated steam.

Anthracene forms colorless plates which when very pure have a slight violet fluorescence. It melts at 213° and boils at about 360°. Alcohol ether and benzene dissolve it sparingly, but the best solvent is hot benzene. With picric acid in it benzene forms the picrate $C_{14}H_{10}C_6H_2(NO_2)_2OH$ which crystallizes in shining red needles melting at 170°. Anthracene is used extensively for the manufacture of the alizarine dyes.

Halogen Compounds of the Hydrocarbons

When chlorine, bromine or iodine act upon a hydrocarbon, benzene for example, a hydrogen atom is taken away and a halogen atom substituted. These products are called substitution derivatives of benzene. For every two atoms of a halogen acting upon benzene, only one becomes attached to the benzene ring, the other is required to remove the hydrogen atom by combining with it to form hydrochloric acid, as shown in the reaction:

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl.$$

Monochlorbenzene, C_6H_5Cl. In most cases, the halogen of the least atomic weight is most energetic, and in the order of their activity they should be arranged, chlorine, bromine, iodine.

In the case of methyl benzene (toluene), $C_6H_5CH_3$, there are two points of attack for chlorine; for example: When chlorine is passed into cold toluene, it replaces hydrogen only in the benzene ring, forming $C_6H_4ClCH_3$, $C_6H_3Cl_2CH_3$, etc., but if the chlorine be passed into boiling toluene, then it is found that only the hydrogens of the methyl-group are

replaced, and we obtain $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$, etc., bodies with very different properties from those formed in the cold.

The following halogen derivatives are of most commercial importance:

Benzyl Chloride, $C_6H_5CH_2Cl$. This compound is formed by leading chlorine on to the surface of the boiling toluene until it has increased in weight 38 per cent. After washing the product with water, it is separated by fractional distillation from any unchanged toluene and from benzylidene chloride and benzotrichloride, which are simultaneously formed. It is a colorless liquid of pungent odor which has a specific gravity of 1.107 at 14° and a boiling point of 178°. By boiling with water and more easily with a solution of K_2CO_3 it is converted into benzyl alcohol, $C_6H_5CH_2OH$.

Benzylidene Dichloride (benzal chloride), $C_6H_5CHCl_2$, is produced by passing chlorine into boiling toluene. It is a colorless oily liquid having a specific gravity of 1.25 at 15° and a boiling point of 206°.

Benzotrichloride, $C_6H_5CCl_3$, is also formed like the two preceding compounds by passing chlorine into boiling toluene: of course the action of the chlorine must continue longer. Its specific gravity is 1.38 at 14° and it boils at 214°. This compound and the last are formed simultaneously and in practice are not separated, but the mixture on heating with milk of lime yields benzaldehyde and benzoic acid. The former coming from the benzalchloride and the latter from the benzotrichloride as follows:

$$\underset{\text{Benzalchloride}}{C_6H_5CHCl_2} + CaO_2H_2 = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + CaCl_2 + H_2O,$$

$$2C_6H_5CCl_3 + 3CaO_2H_2 = 2C_6H_5CO\cdot OH + 3CaCl_2 + 2H_2O.$$

Nitroderivatives of the Hydrocarbons

Nitric acid acts upon the hydrocarbons producing not nitrates but nitro-compounds. The acid removes hydrogen and in its place affixes the nitro-group $-NO_2$ or $-N\overset{O}{\underset{O}{\equiv}}$.

The importance of the nitro bodies is very great, both as intermediate products assisting later in making dyes and as actual dyes themselves. Dilute nitric acid has only an oxidizing action; strong nitric acid substitutes. When the most vigorous action is desired fuming nitric acid is employed, sometimes alone, sometimes with concentrated sulphuric acid. The latter acid simply takes up the water formed in the reaction which otherwise by diluting the nitric acid would diminish its efficiency. The reaction for the nitration of benzene is shown here:

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O.$$

Sulphuric acid is almost always used with nitric acid in manufacturing nitrobenzene: on a large scale 120 parts of nitric acid of specific gravity 1.4 and 180 parts of concentrated sulphuric acid are carefully mixed and allowed to flow slowly with agitation into 100 parts of benzene (thus, by keeping the benzene in excess, avoiding the formation of dinitrobenzene), keeping the temperature below 25° until most of the acid mixture has been added, letting the temperature rise finally to 50°. In practice the operation is carried out in jacketed cast-iron cylinders provided with mechanical stirrers and cooled by a stream of water flowing around them.

If it is desired to form the di- or trinitrobenzene instead of the simple mononitro compound, then the benzene is allowed to flow into the mixture of the nitric and sulphuric acids.

The nitro compounds of benzene are either yellow or nearly colorless; sometimes they are oily liquids, at others crystalline solids. If by reducing agents in an acid solution, the oxygen of the nitro-group is removed, then hydrogen replaces it at once and an amine is formed. No reaction in dye manufacture is carried out upon so large a commercial scale as that of reducing nitrobenzene to aniline.

If instead of an acid solution, an alkaline one be employed, then the nitrobenzene is not converted at once to aniline

but a series of intermediate azoxy, azo, and hydrazo compounds are formed and eventually aniline.

The yield of nitrobenzene from 100 parts of benzene is 150 to 152 parts, thus almost theoretical.

Nitrobenzene is a yellowish oily liquid with an odor resembling benzaldehyde. As a perfume, it was formerly used as essence of mirbane, though of late years its poisonous qualities have lessened the demand. It boils at 206–207° and turns solid on cooling, forming needle-shaped crystals which melt at 5°; the specific gravity is 1.208. Water does not dissolve it, but alcohol and ether dissolve it easily. Nitrobenzene is itself a good solvent for many substances. Nitrobenzene is principally used for the manufacture of aniline. In commerce it is known as "nitrobenzole for blue" or "nitrobenzole for red"; the first is principally used in the manufacture of aniline for blue, and black and induline; the latter is used in preparing aniline for magenta. "Heavy nitrobenzene" consists chiefly of nitrotoluene and nitroxylenes, little true nitrobenzene being present.

Dinitrobenzenes, $C_6H_4(NO_2)_2$. Theoretically, there are three isomeric dinitrobenzenes; all are manufactured from benzene by the action of strong nitric acid upon benzene or nitrobenzene. The meta-compound is formed almost exclusively, little of the ortho or para dinitrobenzene resulting from the reaction.

Metadinitrobenzene, $C_6H_4(NO_2)_2$, is made commercially by allowing 70 parts of nitric acid of specific gravity 1.428 and 100 parts of strong sulphuric acid to run into benzene well agitated, keeping the temperature at 70° at the beginning and allowing it to reach 100° at the end. The resulting product on pouring it into water turns solid, and then it is thoroughly washed.

The pure metadinitrobenzene, easily obtained from the commercial article by recrystallizing from alcohol, forms almost colorless needle-like crystals which melt at 89.8°: the resulting liquid boils at 297°. This dinitrobenzene is chiefly employed in the manufacture of phenylenediamine, which is required for Bismarck brown.

Nitrotoluene, $C_6H_4\begin{cases}CH_3\\NO_2\end{cases}$. The two isomers ortho- and paranitrotoluene are formed simultaneously when 105 parts of nitric of specific gravity 1.4 and 175 parts of strong sulphuric acid are run slowly into 100 parts of well agitated toluene which is carefully kept below 20°. 142 parts of nitrotoluene are produced of which about 63 per cent is ortho, 35 per cent is para and 2 per cent is metanitrotoluene. These may be separated by distillation best under diminished pressure. If the distillation is stopped when 40 per cent have passed over, the distillation is almost pure orthonitrotoluene. The residue on cooling yields crystals of paranitrotoluene which are freed from adhering oils by centrifuging.

Metanitrotoluene, $C_6H_4\begin{cases}CH_3\ (1)\\NO_2\ (3)\end{cases}$ has a melting-point of 16° and a boiling-point of 230–231°.

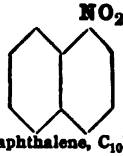
Orthonitrotoluene, $C_6H_4\begin{cases}CH_3\ (1)\\NO_2\ (2)\end{cases}$ is a liquid and boils at 223°.

Paranitrotoluene, $C_6H_4\begin{cases}CH_3\ (1)\\NO_2\ (4)\end{cases}$ melts at 54°, and boils at 238°.

Dinitrotoluenes, $C_6H_3\begin{cases}CH_3\\(NO_2)_2\end{cases}$. The most important isomer of the four theoretically possible dinitrotoluenes is the alpha compound, $C_6H_3\begin{cases}CH_3\ (1)\\NO_2\ (2)\\NO_2\ (4)\end{cases}$. It is prepared in the same manner as nitrotoluene except that the acid mixture is hot. It forms long yellowish needles which melt at 60°.

Nitroxylenes, $C_6H_3(CH_3)_2NO_2$. Of the six isomeric nitroxylenes which according to the theory may be formed, one is of especial technical importance, and this is the alpha-metanitroxylene, $C_6H_3(CH_3)_2NO_2 \cdot 1:3:4$. A mixture of 90 parts of nitric acid of specific gravity 1.4 and 150 parts of strong sulphuric acid is run into 100 parts of metaxylene, rapidly

agitated and kept below 17° until most of the acid has been added. It is a light yellow liquid boiling at 245° and having a specific gravity of 1.126 at 17°. The product sold in commerce is usually a mixture of isomers having nitrometa-xylene as its chief constituent. Without separation the product is converted into xylidine.



Nitronaphthalene, $C_{10}H_7NO_2$

Nitronaphthalene is prepared by sprinkling 250 parts finely ground naphthalene slowly into a mixture of 200 parts of nitric acid of specific gravity 1.375, 200 parts of concentrated sulphuric acid together with 600 parts of acid from previous nitrations. The mixture is kept constantly agitated and at a temperature from 45° to 50°. When the mixture has become cold, the nitronaphthalene forms a solid cake from which the acids are run off. The solid product is washed with hot water, and if wanted quite pure it is melted with one-tenth of its weight of "solvent naphtha," filtered, and the crystalline cake formed on cooling is subjected to hydraulic pressure.

It forms long fine needles which melt at 61° and boil at 304°. Alcohol and benzene dissolve it easily.

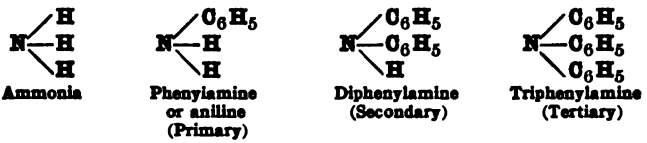
CHAPTER IV

THE HYDROCARBONS AND THEIR DERIVATIVES—*Continued*

Aminoderivatives of the Hydrocarbons

The entrance of nitrogen into the hydrocarbons brings them at once nearer to the rank of dyes. Of all the compounds of nitrogen known to the dye manufacture, none are of so great importance as the amines. These bodies may be regarded as substituted ammonias: a molecule of ammonia (NH_3), in which one, two, or all three of the hydrogen atoms may be replaced by organic radicals, forms an amine. In the amine, the character of ammonia is retained to a large degree; the amines form salts with acids the same as ammonia itself.

The amines divide themselves into three classes, according to the number of hydrogen atoms which have been replaced. Primary amines have one hydrogen replaced, secondary two, and tertiary three. The following structural formulas show the relations of the three classes to each and to ammonia:



In the place of phenyl ($—C_6H_5$), any other organic radical may be substituted: e.g., methyl ($—CH_3$), ethyl ($—C_2H_5$), etc.

The group $—NH_2$ occurring in the primary amines is known as the amino group. Aniline is often called either aminobenzene or phenylamine. The group (=NH) of the secondary amines is known as the imino group.

Nitrogen in these compounds is always in combination with carbon and hydrogen.

The entrance of two or three amino-groups into the same benzene ring gives rise to primary *diamines* or *triamines*, e.g., $C_6H_4(NH_2)_2$ phenylene diamine; $C_6H_3(NH_2)_3$ triaminobenzene.

The nitro compounds of the hydrocarbons of the aromatic group generally form the starting point for the amines. Reduction of the nitro-group by nascent hydrogen produces the amines directly,

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H = \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O.$$

The nascent hydrogen may be produced in a variety of ways: 1. By hydrochloric acid acting on either tin or iron. 2. By acetic acid on iron. 3. By hydrogen sulphide acting upon nitro compounds in ammoniacal solution.

Iron and hydrochloric acid are chiefly employed on a manufacturing scale for complete reduction, while partial reduction is effected by hydrogen sulphide.

Aniline, $C_6H_5NH_2$. Aniline was discovered many times by independent investigators and it received a different name from each discoverer. Unverdorben first discovered it in 1826 by the dry distillation of indigo, and named it "crystalline" because of the marked crystallizing power of its salts. Runge obtained it from coal-tar in 1834 and named it cyanole from the blue color it yields with a solution of bleaching powder. Zinin prepared aniline in 1841 by the action of ammonium sulphide on nitrobenzene and called it "benzidam." In the same year, Fritzsche in distilling indigo with caustic potash, obtained a base which he called aniline, from anil, the Portugese name of indigo. A. W. Hoffman in 1843 proved that all these four were one and the same substance which we know to-day as aniline.

Aniline was the first substance to be transformed into a dyestuff, when in 1856 Perkin heated it with sulphuric acid and bichromate of potash, obtaining the celebrated mauve, used until the end of the last reign for coloring the English postage stamps.

Aniline is present in coal-tar, but in quantities too small to pay for extracting it. It is manufactured by reducing nitrobenzene with hydrogen which is evolved from iron filings and one-fortieth the amount of hydrochloric acid required by the following equation.

$$C_6H_5NO_2 + 2Fe + 6HCl = C_6H_5NH_2 + 2FeCl_3 + 2H_2O.$$

This interesting process, whereby a certain amount of hydrochloric acid may accomplish forty times the amount of chemical work that would ordinarily be expected of it in transforming nitrobenzene into aniline, may be explained as follows:

The first action of iron filings, hydrochloric acid, and nitrobenzene would appear thus:

$$(1)\quad C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 3FeCl_2 + 2H_2O.$$

Then the ferrous chloride reacting with more acid would become ferric chloride and furnish more of the requisite hydrogen for the reduction of another molecule of nitrobenzene:

$$(2)\quad C_6H_5NO_2 + 6FeCl_2 + 6HCl = C_6H_5NH_2 + 6FeCl_3 + 2H_2O.$$

These two reactions would continue as long as the free acid lasted which would not be for long; because the aniline formed would begin to exhaust it by uniting with it producing aniline hydrochloride $C_6H_5NH_2 \cdot HCl$.

This aniline hydrochloride, however, in the presence of nitrobenzene and iron behaves exactly as hydrochloric acid and the aniline is set free:

$$(3)\quad 6C_6H_5NH_2 \cdot HCl + 3Fe + C_6H_5NO_2 = 7C_6H_5NH_2 + 3FeCl_2 + 2H_2O.$$

$$(4)\quad 6C_6H_5NH_2 \cdot HCl + 6FeCl_2 + C_6H_5NO_2 = 6C_6H_5NH_2 + C_6H_5NH_2 + 6FeCl_3 + 2H_2O$$

The molecules of aniline set free, together with the one formed simultaneously from the molecule of nitrobenzene, then react with the ferric chloride and water, reforming aniline chloride and turning the iron salt into an oxide:

$$(5) \quad 6C_6H_5NH_2 + 2FeCl_3 + 3H_2O = 6C_6H_5NH_2 \cdot HCl + Fe_2O_3.$$

The aniline hydrochloride is again ready to act upon iron filings as in reaction (3) setting more hydrogen free to act upon another molecule of nitrobenzene.

According to the theory, therefore, the reactions (3), (4), and (5), may repeat themselves indefinitely. A small amount of hydrochloride acid to bring the process up to this phase is all that is needed, and with additional iron filings and water is thus able to transform an unlimited quantity of nitrobenzene into aniline.

Aniline is a colorless oily liquid, of a peculiar odor, which turns brown on exposure to light and air. Water will dissolve about 3 per cent, and aniline in turn takes up 5 per cent of water. It has a specific gravity of 1.0261 at 15° and boils at 184°; when once solidified by cold it melts at 8°.

Aniline mixes in all proportions with alcohol, ether, and many other ordinary solvents, and it is itself a solvent for indigo, sulphur and phosphorus. When taken internally the oil, which has a burning taste, is poisonous. The vapor, when inhaled, acts similarly, causing a dangerous illness (anilisme), which is not uncommon in aniline works. Aniline has no action on litmus.

Ammonia expels aniline from its salts in the cold, but on heating ammonium salts with aniline, ammonia is set free, because of its greater volatility. Aniline is easily affected by oxidizing agents: the resulting products being of great importance to the dye industry. A solution of bleaching powder causes a solution of aniline to assume a violet color. A drop of aniline added to sulphuric acid and a little potassium bichromate produces first a red color and finally a deep blue.

Commercial "aniline oil" appears in commerce in four different grades which are known as,

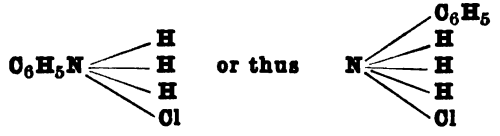
1. Aniline oil for blue and black;
2. Aniline oil for red (magenta);
3. Aniline oil for safranine;
4. Liquid toluidine.

The first contains almost pure aniline, that for red is made up of 30 per cent aniline, 35 per cent orthotoluidine, and 35 per cent paratoluidine; that for safranine contains varying amounts of aniline and orthotoluidine. Liquid toluidine is a mixture of ortho- and paratoluidine.

Aniline is a basic compound and easily forms salts with acids. As a derivative of benzene it may be regarded as aminobenzene: as a derivative of ammonia, it is looked upon as phenylamine. Since aniline exhibits the properties of both benzene and ammonia, a good understanding of the reaction of which it susceptible requires that both aspects should be constantly kept in mind.

Aniline Salts. If a few drops of any of the common mineral acids are brought into contact with aniline upon a watch glass, solidification to a white opaque mass instantly results with the formation of a salt.

Aniline Hydrochloride, $C_6H_5NH_2HCl$. Of all the aniline salts the hydrochloride is most important. The nitrogen in aniline is trivalent and in the aniline salts it becomes pentavalent and the formula of the hydrochloride may be represented graphically thus:



Aniline hydrochloride Aniline hydrochloride

Pure aniline (100 parts), with concentrated hydrochloric acid (130–135 parts) is mixed in strong stoneware vessels. The salt is allowed to crystallize out and it is freed from the mother liquors by centrifugal force. Aniline hydrochloride

forms colorless crystals easily dissolved by water and alcohol, which sublime at 192° C. It is largely used in the dyeing and printing of aniline black.

Acetanilide, $C_6H_5NH \cdot C_2H_3O$. If aniline is simply mixed with glacial acetic acid, aniline acetate is formed. This salt breaks up on boiling for some hours, water is eliminated and acetanilide results:

$$\underset{\text{Aniline acetate}}{C_6H_5NH_2 \cdot C_2H_4O_2} = \underset{\text{Acetanilide}}{C_6H_5NH(C_2H_3O)} + H_2O.$$

This substance is the antifebrin of medicine which is used as an antipyretic and antirheumatic. It forms colorless crystals which melt at 112° C. and the resulting liquid boils at 295° C. Acetanilide was used in the manufacture of flavaniline.

Diaminobenzenes, $C_6H_4(NH_2)_2$

Just as the single nitro group of nitrobenzene is reduced by nascent hydrogen to an amino group, thereby forming aminobenzene or aniline, so the pairs of nitro groups in the dinitrobenzenes are likewise reduced by hydrogen to amino groups. Three dinitrobenzenes are known and by reduction with iron and hydrochloric acid, three corresponding diaminobenzenes are formed.

Metadiaminobenzene. Of these three compounds the metadiaminobenzene is the most important, and it is formed by the complete reduction of ordinary (meta) dinitrobenzene. It forms colorless crystals which melt at 63° and boil at 287°. By easily dissolving in water, it is distinguished from dinitrobenzene from which it is made. Metadiaminobenzene is employed for the manufacture of chrysoidine and Bismarck brown.

Paradiaminobenzene or paraphenylenediamine is not made from the corresponding paradinitrobenzene but from paranitroacetanilide by reduction. It is a crystalline substance which melts at 147° C. and dissolves easily in water. If it is melted with sulphur, then a thio-compound is formed which gives by oxidation Lauth's violet.

Aminotoluenes or Toluidines, $C_6H_4\begin{cases}CH_3\\NH_2\end{cases}$

Three isomeric toluidines are known. They resemble aniline very closely and they may be obtained from the three corresponding nitrotoluenes. However, on treating toluene with nitric acid, chiefly ortho- and paranitrotoluene are formed and very little of the meta compound. Hence, by reducing the nitrotoluenes to aminotoluenes or toluidines only the ortho and para derivatives are formed to any extent. From its scarcity and high cost, the metatoluidine is not employed in dye manufacture.

The orthotoluidine is separated from the paratoluidine by treating the mixed bases with sulphuric acid insufficient to fully neutralize them and then distilling. The stronger para base remains behind as sulphate.

According to another method, the mixture of bases is neutralized with hydrochloric acid and mixed with an excess of sodium phosphate. The mass solidifies to a crystalline paste which dissolves on heating; the orthotoluidine floats as an oily layer on the surface and is removed. When the aqueous solution cools, paratoluidine separates out completely while a little phosphate of orthotoluidine remains dissolved in the mother liquor. The bases are now set free from their salts by caustic soda, when the sodium phosphate is recovered.

Orthotoluidine, $C_6H_4\begin{cases}CH_3\ (1)\\NH_2\ (2)\end{cases}$, is a colorless liquid which becomes brown on exposure to light and air. It has about the same solubility as aniline. Its boiling point is 197° C. and its specific gravity at 15° is .9978. Orthotoluidine is found in all commercial aniline oils excepting "aniline for black." Pure orthotoluidine is employed for making some azo dyes.

Metatoluidine, $C_6H_4\begin{cases}CH_3\ (1)\\NH_2\ (3)\end{cases}$, forms a colorless oil boiling at 199° C. It is too costly for use in dye manufacture.

Paratoluidine, $C_6H_4\begin{cases}CH_3\ (1)\\ NH_2\ (4)\end{cases}$, is a solid substance forming leaf-shaped crystals melting at 45° C.; it boils at 198° C. In the water it is slightly soluble, but in alcohol and ether it dissolves with ease. Large quantities of paratoluidine are used for the manufacture of magenta.

Aniline Oils Containing Toluidine

Aniline Oil for Red. The aniline used for manufacturing rosaniline is not a simple substance but a mixture of three, aniline, orthotoluidine and paratoluidine. One molecule of each in proportion is employed.

Aniline Oil for Safranine. This aniline is a by-product of the rosaniline manufacture, and it is the distillate recovered from the rosaniline melt. Little paratoluidine is present, and it consists principally of aniline and orthotoluidine.

Toluylenediamines, $C_6H_3(CH_3)(NH_2)_2$. When, in the case of benzene, two nitro groups were substituted for two hydrogens, three isomeric nitrobenzenes were formed and by their reduction three aminobenzene or phenylenediamines resulted. If two nitro groups are substituted for hydrogen in toluene the next higher homologue of benzene, not only three but six isomeric dinitrotoluenes would be expected theoretically, and all in fact are known. Of these six, alpha-toluylenediamine is the most important and its composition is shown by the formula,

$$C_6H_3\begin{cases}CH_3\ (1)\\ NH_2\ (2)\\ NH_2\ (4)\end{cases}$$

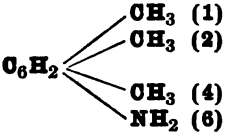
Alpha-toluylenediamine

It is formed by reducing the dinitrotoluene (1, 2, 4). It is a colorless crystalline substance melting at 99° C. and dissolving easily in water. Use is made of it in producing chrysoidine and Bismarck brown.

Aminoxylenes, or **Xylidenes,** $C_6H_3(CH_3)_2(NH_2)$. The six isomeric xylidines which are theoretically possible are all known. Two are obtained from orthoxylene, three from meta-

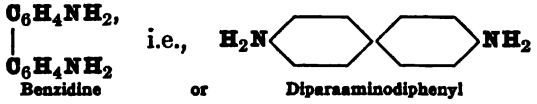
xylene and one from paraxylene. The xylidine of commerce is a mixture to a greater or less extent of all six, but about 50 per cent is the aminoorthoxylene (1, 3, 4). Xylidine is an oily liquid boiling between 211–219° C., and it is employed principally for the manufacture of the azo dyes.

Cumidine. By heating paraxylidine with methyl alcohol in closed vessels to 300° C. one methyl group is substituted for one of the hydrogens in the ring. The result is cumidine:



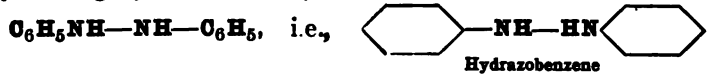
Cumidine

BENZIDINE (DIPARAAMINODIPHENYL)



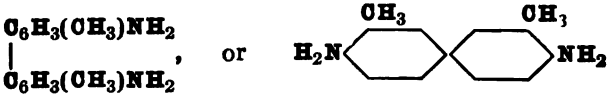
Benzidine or Diparaaminodiphenyl

This substance aroused no practical interest at the time of its discovery by Zinin in 1845 and it was not until nearly forty years later in 1884 that through the discovery of Congo red, it became of commercial importance. It may be obtained by boiling hydrazobenzene,



Hydrazobenzene

with hydrochloric acid, after which the solution is filtered and the benzidine precipitated by sulphuric acid or sodium sulphate. The pure base is obtained by decomposing the sulphate with caustic soda and distilling. Pure benzidine forms large colorless silky plates which melt at 122° C. and boil above 360° C. It is slightly soluble in cold water. It is used in the preparation of cotton azo colors.



Tolidine (Diparaamidonitolyl)

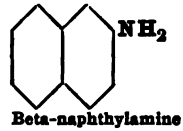
Tolidine is manufactured by reducing orthonitrotoluene by zinc dust and caustic soda; the resulting hydrazotoluene is then converted into tolidine by boiling with hydrochloric acid and purifying by a method similar to that used in benzidine.

It forms glistening plates which melt at 128° C. It dissolves slightly in water and easily in alcohol. The sulphate, though sparingly soluble, dissolves more easily than benzidine sulphate.

Naphthylamines or **Aminonaphthalenes, $C_{10}H_7NH_2$.** Both the isomeric naphthylamines, theoretically possible are known and both are commercially important.

Alpha-naphthylamine, results when alpha-nitronaphthalene is reduced by iron and hydrochloric acid. Of a basic nature, it combines with acids to form salts. The aqueous solution of these salts, by treatment with mild oxidizing agents, yields a blue precipitate called naphthamein. Alpha-naphthylamine is required for the manufacture of the azo dyes, e.g., naphthol yellow and magdala red. It forms colorless crystals of a disagreeable odor which melt at 50° C. and have a boiling point of 300° C.

BETA-NAPHTHYLAMINE



Beta-naphthylamine

The nitrogen of the amino group of this compound is not furnished by nitric acid acting upon naphthalene as in the preceding instance. It is supplied by ammonia, when betanaphthol is heated with ammonia to a high temperature in closed vessels. The reaction appears in the following equation:

$$\underset{\text{Beta-naphthol}}{C_{10}H_7OH} + NH_3 = \underset{\text{Beta-naphthylamine}}{C_{10}H_7NH_2} + H_2O.$$

Beta-naphthylamine amine is prepared on a manufacturing scale by heating in a closed vessel at 160° C., 10 parts of beta-naphthol, 4 parts of caustic soda, and 4 parts of ammonium

chloride. The heating continues for 69–70 hours. The cold melt is pulverized, the unchanged β-naphthol is extracted by the use of aqueous caustic soda, and the pure residue is dissolved in hydrochloric acid. The solution is filtered and then treated with soda, which decomposes the soluble salt and precipitates the β-naphthylamine.

β-Naphthylamine forms white pearly plates which in the commercial product are compacted into pinkish white pearly lumps, almost without odor. It is slightly soluble in cold water but easily soluble in hot water, alcohol, and ether. The pure substance forms colorless and odorless crystals which melt at 112°. The demand for β-naphthylamine arises in the manufacture of red azo dyes.

Secondary Amines

The secondary amines may be regarded as substituted ammonia, i.e., a molecule of ammonia in which two hydrogen atoms have been replaced by organic radicals. For our present purpose aniline is chosen as the starting point. Aniline may be regarded as ammonia in which one hydrogen atom has been replaced by the organic radical phenyl. There are two important methods of producing the secondary amines.

First. A primary amine is heated with the hydrochloride of the same amine, e.g., aniline is heated with aniline hydrochloride,

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\substack{\text{Aniline}\\ \text{hydrochloride}}}{C_6H_5NH_2HCl} = NH_4Cl + \underset{\substack{\text{Diphenylamine.}\\ \text{(Secondary amine)}}}{NH(C_6H_5)_2}$$

Second. By heating together primary aromatic amines with the halogen compounds of the alcohol radicals.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CH_3Cl = HCl + \underset{\text{Methylaniline}}{NH(CH_3)C_6H_5}$$

Tertiary Amines

All three hydrogen atoms of ammonia are capable of replacement by organic radicals. When they are so replaced, tertiary amines are formed. To prepare a tertiary amine of the

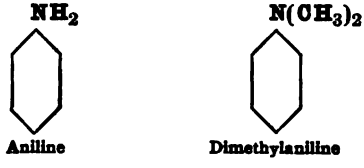
aromatic series, primary amines are heated with the chlorides of methyl, ethyl, propyl, etc.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + 2\underset{\substack{\text{Methyl}\\\text{Chloride}}}{CH_3Cl} = \underset{\substack{\text{Dimethylaniline.}\\\text{(Tertiary amine)}}}{C_6H_5(CH_3)_2N} + 2HCl$$

The same result is attained by heating the hydrochlorides of the amines with the alcohols and zinc chloride.

$$\underset{\substack{\text{Aniline}\\\text{hydrochloride}}}{C_6H_5NH_2HCl} + 2C_2H_5OH = \underset{\text{Diethylaniline}}{C_6H_5(C_2H_5)_2N} + HCl + 2H_2O$$

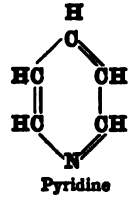
Dimethylaniline, $C_6H_5N(CH_3)_2$. For the manufacture of dimethylaniline, 75 parts of aniline, 25 parts of aniline hydrochloride and 75 parts of methyl alcohol (acetone free) are heated under pressure in a cast-iron autoclave at 230–270° C. This is carefully kept under six atmospheres. From the above proportions the yield is about 120 parts. The product is purified by distillation.



Aniline Dimethylaniline

Pyridine Bases

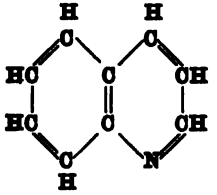
Coal-tar contains, together with the various hydrocarbons, bodies of a basic nature containing nitrogen. Of these bases, pyridine in the simplest example. It is closely related to benzene since its structure resembles that of the benzene with this important exception that one of the carbon atoms and its combined hydrogen is replaced by a nitrogen atom. The following formula makes this relation clear:



Pyridine

Pyridine is also found in Dippel's oil, which is produced by the distillation of bones. It is a colorless liquid of a penetrating disagreeable odor. In Germany it is much used for denaturing alcohol. Methylpyridine, its methyl homologue called picoline, forms theoretically three isomers, all three of which are known.

Quinoline, C_9H_7N. If one of the α-carbon atoms of naphthalene with its hydrogen be considered as replaced by nitrogen, a new base quinoline would result. The formula exhibits its relation to naphthalene, in which it may be seen to exhibit the relation which pyridine bears to benzene:



Quinoline

It is a constituent of coal-tar. It may be separated from that part of the heavy oil which dissolves in sulphuric acid. Skraup suggested a successful method for its synthetical formation in which aniline, glycerine and sulphuric react in the presence of nitrobenzene:

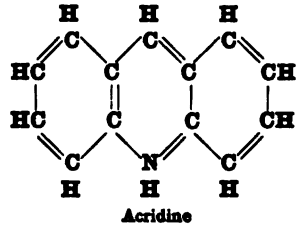
$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Glycerine}}{C_3H_5(OH)_3} + O = \underset{\text{Quinoline}}{C_9H_7N} + 4H_2O$$

It is an oily liquid without color, which boils at 238° C. and possessing a specific gravity of 1.094 at 20°. With the acids it forms salts of well-marked characteristics.

Use is found for quinoline in the manufacture of quinoline blue, quinoline red, and quinoline yellow.

Acridine occurs in the anthracene obtained from coal-tar, and it has also been prepared synthetically. It resembles anthracene in its general structure and it may be regarded as anthracene in which one of the middle carbons with its

attached hydrogen has been replaced by a nitrogen atom. The formula shows its relation to anthracene:



Acridine

The acridines are very stable bodies but they are more feeble bases than the pyridines and quinolines. It melts at 11° C. and sublimes at 100° C. A blue fluorescence is characteristic of its solutions.

Diazo Compounds

These are nitrogenous compounds of the aromatic series. The syllable azo (from the French azote-nitrogen) signifies a nitrogenous composition. In all these substances the characteristic group of two nitrogen atoms doubly bound to each other occurs represented as follows:

$$—N{=}N— \quad \text{or} \quad —N{:}N—$$

On one side this group is bound to the carbon atom of a benzene, naphthalene or other ring compound: the other side is attached to an acid or basic radical: as the following formula shows:

$$C_6H_5—N{:}N—Cl$$

Diazobenzene chloride

Such compounds were first produced by the action of nitrous fumes (N_2O_3) upon aniline. Thus it will be seen that one nitrogen atom in the amino group of aniline is attached to a carbon of the benzene ring while nitrous acid contributes the second requisite nitrogen atom. The nitrous fumes (from arsenious oxide and nitric acid)

$$As_2O_3 + 2HNO_3 = N_2O_3 + H_2O + As_2O_5$$

passed into a cold aqueous solution of an aniline salt converts the aniline into a salt of diazobenzene as shown below: the nitrous fumes in the water solution behaving as nitrous acid:

$$\underset{\text{Aniline hychloride}}{C_6H_5NH_2HCl} + \underset{\text{Nitrous acid}}{HONO} = \underset{\text{Diazobenzene chloride}}{C_6H_5N{:}NCl} + 2H_2O$$

In practice the nitrous acid is formed in the cold solution of aniline salt itself by adding the requisite amount of sodium nitrite and the necessary amount of acid to decompose it, forming nitrous acid in the immediate presence of the aniline salt: the nitrous acid being generated as follows:

$$NaNO_2 + HCl = HNO_2 + NaCl,$$

or

$$2NaNO_2 + H_2SO_4 = 2HNO_2 + Na_2SO_4$$

Different observers have ascribed different structural formulas to diazobenzene salts, the latter of the two given below being the more commonly accepted:

$C_6H_5N{:}NCl$

Diazobenzene chloride

Kekule Z. f. Ch. N.F. (1866), 2, 308: Chemie der Benzolderivate.

or

$C_6H_5N{\equiv}N$ (Cl)

Diazobenzene chloride

The view of Bloomstrand, A. Strecker and E. Erlenmeyer.

In the manufacture of the diazobenzene salts, ice is used to reduce the temperature of the solution of the aniline salt, during the addition of the nitrite and acid; for, if the temperature rises beyond a certain point, the compound decomposes and all the nitrogen escapes and may be seen rising in bubbles through the liquid.

The diazo compounds are very unstable, some dangerously explosive when dry, especially the nitrates. Consequently they are seldom prepared in the dry state: they are used in the cold solution where they have been formed, and are converted then and there into the oxyazo or aminoazo dyes for which they are required.

If the solution in which these salts are formed be boiled

all the nitrogen escapes and the corresponding phenols are left behind:

$$\underset{\text{Diazobenzene chloride}}{C_6H_5N:NCl} + H_2O = \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

By heating the solution with the salts of amino compounds, aminoazo compounds are produced from the diazo compounds, e.g.,

$$\underset{\text{Diazobenzene chloride}}{C_6H_5N:NCl} + \underset{\text{Aniline hydrochloride}}{C_6H_5NH_2HCl} = \underset{\text{Aminoazobenzene hydrochloride}}{C_6H_5N:NC_6H_4NH_2HCl} + HCl$$

If phenols in alkaline solution be added to the diazo solution, oxyazo compounds are produced,

$$C_6H_5N:NCl + C_6H_5OK = C_6H_5N:NC_6H_4OH + KCl$$

Great importance attaches to the last two reactions in azo dye manufacture.

Hydrazines

The hydrazines are derivatives of the substance known as diamine or hydrazine $H_2N:NH_2$. These derivatives were known long before the hydrazine itself had been isolated. Of commercial importance is

Phenylhydrazine, $C_6H_5NH:NH_2$. This substance has been of extraordinary service in the study of the sugars. It may be made by reducing diazobenzene chloride with sodium sulphite and zinc dust or stannous chloride in acid solution,

$$\underset{\text{Diazobenzene chloride}}{C_6H_5N:NCl} + 4H = \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5NH:NH_2} + HCl$$

From this salt, sodium hydroxide sets free the phenylhydrazine,

$$\underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5NH:NH_2HCl} + NaOH = \underset{\text{Phenylhydrazine}}{C_6H_5NH:NH_2} + NaCl + H_2O$$

When pure and kept out of contact with the air, it is a colorless aromatic oil of poisonous properties. It forms plate-like crystals which melt at 23°, and it boils at 241–242° with slight decomposition. It is the important source of antipyrine: and it is a valuable reagent for detecting aldehydes and ketones.

The Azo Compounds

The azo compounds resemble the diazo compounds in containing the double nitrogen group, —N:N—, but in the azo compounds two benzene rings are present, one at each end of the double nitrogen group. The simplest of these substances is azobenzene, $C_6H_5—N:N—C_6H_5$.

If nitrobenzene is reduced by nascent hydrogen in an acid solution, aminobenzene or aniline is formed; but, if the reduction is carried out in an alkaline solution, azobenzene is one of the products. Such an alkaline solution is furnished by zinc dust and sodium hydroxide, or by stannous chloride and sodium hydroxide,

$$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} + 8H = \underset{\text{Azobenzene}}{C_6H_5N:NH_6H_5} + 4H_2O$$

The azo compounds are much more stable than the diazo compounds. Boiling them in the solution in which they are formed either in the presence of acids or alkalies does not decompose them nor are they explosive in the dry state. Some may be distilled unchanged.

Mild reducing agents convert azobenzene into hydrazobenzene as follows:

$$\underset{\text{Azobenzene}}{C_6H_5N:NC_6H_5} + 2H = \underset{\text{Hydrazobenzene}}{C_6H_5NH—NHC_6H_5}$$

More energetic reduction fixes more hydrogen and causes a break between the two nitrogen atoms, converting each into an amino group and forming two molecules of aniline.

$$\underset{\text{Azobenzene}}{C_6H_5N:NC_6H_5} + 4H = \underset{\text{Aniline}}{2C_6H_5NH_2}$$

By such a reduction aminoazobenzene would yield a monamine (e.g., aniline), and a diamine (e.g., phenylene diamine, $C_6H_4(NH_2)_2$,

$$\underset{\text{Aminoazobenzene}}{C_6H_5N:NC_6H_4NH_2} + 4H = \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Phenylenediamine}}{C_6H_4(NH_2)_2}$$

Oxyazo compounds by a similar reduction would produce a monamine and an aminophenol.

$$\underset{\text{Oxyazobenzene}}{C_6H_5N:NC_6H_4OH} + 4H = \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Aminophenol}}{C_6H_4NH_2(OH)}$$

These reactions are of value in determining the composition of the azodyes.

The Sulphonic Acids; or Sulpho Acids

When the aromatic hydrocarbons are treated with concentrated sulphuric acid, a new class of substances termed sulphonic acids is formed. The hydrocarbon loses only an atom of hydrogen, while the acid loses a hydroxyl —OH group, the two forming a molecule of water and the sulphonic acid in question. The sulphonic acid group is $-SO_3H$. These acids are formed by heating together concentrated sulphuric acid and a hydrocarbon. Such action is called sulphonation. Fuming sulphuric acid is sometimes used for this purpose. A higher temperature or longer heating forms both mono and disulphonic acids,

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 = \underset{\substack{\text{Benzene}\\\text{monsulphonic acid}}}{C_6H_5SO_3H} + H_2O$$

$$\underset{\text{Benzene}}{C_6H_6} + 2H_2SO_4 = \underset{\substack{\text{Benzene}\\\text{disulphonic acid}}}{C_6H_4(SO_3H)_2} + 2H_2O$$

Of the three possible disulphonic acids of benzene itself, the meta and para compounds are those obtained by this method. The ortho benzene disulphonic acid is formed from meta aminobenzene sulphonic acid by the further introduction of a sulpho group and the replacement of the amino ($-NH_2$) group by hydrogen.

Amines and phenols yield themselves more readily to form sulphonic acids than do the hydrocarbons themselves. Sometimes the amino sulphonic acid may be obtained by simply heating the sulphate of the amino compound to 180° C. The free sulphonic acids are as a matter of fact less frequently prepared than the sodium salts of the same which are termed sulphonates. The following general method will indicate the process.

The hydrocarbon and the strong or fuming sulphuric acid are heated together until the evolution of sulphur dioxide shows that oxidation with consequent destruction of some of the substances is taking place. The product containing an excess of sulphuric acid is poured into water. Then, by the addition of barium carbonate, chalk, or milk of lime the acid is neutralized and precipitated: the sulphonic acid combines with the lime to form a soluble lime salt. The liquid is filtered and the soluble lime salt in the filtrate is changed into a sodium salt by the addition of sodium carbonate, which precipitates calcium carbonate and leaves a soluble sodium sulphonate in the solution. The liquid is filtered off and evaporated to dryness.

The following reactions have taken place:

$$\underset{\text{Benzene sulphonic acid}}{2C_6H_5SO_3H} + CaO_2H_2 = 2H_2O + \underset{\text{Benzene monosulphonate of calcium}}{(C_6H_5SO_3)_2Ca}$$

$$(C_6H_5SO_3)_2Ca + Na_2CO_3 = 2C_6H_5SO_3Na + CaCO_3$$

Pure sulphonic acids do not crystallize well nor do they have definite melting or boiling points and they are usually deliquescent. They may be sufficiently characterized, however, by converting them into chlorides or amides. The chlorides are obtained by allowing phosphorus pentachloride to act upon the free sulphonic acids:

$$C_6H_5SO_3H + PCl_5 = C_6H_5SO_2Cl + HCl + POCl_3$$

The amides are formed by ammonia acting upon the chlorides:

$$C_6H_5SO_2Cl + NH_3 = C_6H_5SO_2NH_2 + HCl$$

Benzene Monosulphonic Acid, $C_6H_5SO_3H$, forms colorless crystals which dissolve easily in water and alcohol. Caustic soda at a high temperature converts it into phenol C_6H_5OH. Concentrated nitric acid changes the phenol into nitrophenol and nitrous acid in aqueous solution changes phenol into nitroso-phenol.

Benzene Disulphonic Acids, $C_6H_4(SO_3H)_2$. Three isomers are possible and all are known. The direct action of fuming sulphuric on benzene or benzene monosulphonic acid produces a mixture of two of the isomers, the meta- and para-disulphonic acids. Large quantities of this mixture of isomers are prepared for the manufacture of resorcin: sometimes by passing the vapor of benzene into strong sulphuric acid heated to 240° C. or 1 part of benzene may be dissolved in 4 parts of fuming sulphuric acid and then the solution is heated for two hours at 275° C. When these products are fused with caustic soda both the meta- and para-disulphonic acids are converted into resorcin (metadioxybenzene), $C_6H_4(OH)_2$.

Naphthalene Monosulphonic Acids, $C_{10}H_7SO_3H$. Naphthalene, like benzene, yields to treatment of strong sulphuric acid, forming sulphonic acids by the replacement of hydrogen atoms by the groups ($—SO_3H$). Unlike benzene, however, naphthalene forms two different sulphonic acids by the entrance of only one sulphonic group into its molecule. The difference depends upon the position of the hydrogen atom which is replaced by the ($—SO_3H$) group. These two isomers are known as α- and β-naphthalene monosulphonic acids.

By the simple regulation of the temperature one or the other of these isomers may be produced in excess. Thus, by carrying on sulphonation at 100° C. the product contains about 80 per cent of the α-sulphonic acid and 20 per cent of the β acid, but if the temperature be raised to 160–170° C. only 25 per cent of the α acid will be formed, but 75 per cent of the β acid will be produced.

α-Naphthalene Sulphonic Acid, $C_{10}H_7SO_3H$, is manufactured by stirring 1 part of finely powdered naphthalene

into 2 parts of strong sulphuric acid at 40° C. and keeping it for several hours at this temperature (Ger. Pat.). The product is dissolved in water, filtered from any unchanged naphthalene, and the soluble sodium sulphonate is precipitated by the addition of salt.

The α acid forms deliquescent crystals which melt at 85–90° C. By heating it is converted into the β-naphthalene sulphonic acid. Its salts are more soluble than those of the β acid.

β-Naphthalene Sulphonic Acid, $C_{10}H_7SO_3H$, is formed by heating 1 part of naphthalene with 1 part of concentrated sulphuric acid to 180° C. for several hours. The resulting product is dissolved in water and some dinaphthylsulphone filtered off, when the sodium salt may be precipitated by adding common salt. Its crystals take the form of plates and do not deliquesce.

Nitrosulphonic Acids. These acids possess both the nitro ($—NO_2$) group and the sulphonic acid group ($—SO_3H$). In converting benzene, for example, into benzenenitro sulphonic acid, the benzene may be first nitrated by strong nitric acid and then sulphonated; or the operations may be reversed, first forming a benzene sulphonic acid and then nitrating this. The chief product is that one of the three possible isomers which are called metanitrobenzene sulphonic acids.

Naphthalene Disulphonic Acids
$C_{10}H_6(SO_3H)_2$

By controlling the strength of the sulphuric acid used and the various other conditions, two sulphonic acid groups may become attached to the naphthalene molecule forming naphthalene disulphonic acids. Ten isomers of disulphonic acids are possible and all are known. Of these the two following show the methods used:

Naphthalene Disulphonic Acid (1:5). Armstrong's Delta (δ) Acid, is made by adding 1 part of finely powdered naphthalene to 4 parts of fuming sulphuric acid containing 30 per cent of SO_3 and keeping the temperature as low as possible. By

dissolving the product in 3 or 4 times its weight of salt solution, the sodium salt separates out, and the isomers simultaneously formed remain in solution. (Ger. Pat.) It crystallizes in glistening white plates.

Naphthalene Disulphonic Acid (2:6). Ebert and Merz's β Acid. This acid is produced on heating 1 part of naphthalene with 5 parts of concentrated sulphuric acid to 180° C. for 24 hours. By maintaining these conditions, this acid is formed almost exclusively. It crystallizes in plates and the sodium salt forms needles containing one molecule of water.

Amino Sulphonic Acids

These derivatives of the hydrocarbons contain both the amino group (—NH_2) and the sulphonic acid group (—SO_3H). In some processes of manufacture, the amino group will be put into the molecule first, in others, the sulphonic acid group; as may be seen from the following methods:

1. Direct action of sulphuric acid on the amines.

2. By simply heating the sulphates of the amines to 180–230° C., e.g.,

$$\underset{\text{Aniline sulphate}}{(C_6H_5NH_2)_2H_2SO_4} + \text{Heat} = C_6H_4(NH_2)SO_3H + H_2O + C_6H_5NH_2$$

Aminobenzene sulphonic acid

3. By heating a sulphonic acid with nitric acid, thus forming a nitro sulphonic acid, and then by reduction converting the nitro group into an amino group.

Aminobenzene Sulphonic Acids, $C_6H_4\begin{cases}NH_2\\SO_3H\end{cases}$. The three isomers theoretically possible are all known: the meta- and para-compounds being of the greatest technical value.

Metaaminobenzene Sulphonic Acid, $C_6H_4\begin{cases}NH_2\ (1)\\SO_3H\ (3)\end{cases}$, is made by the action of nascent hydrogen, evolved from iron and dilute sulphuric acid, upon nitrobenzene sulphonic acid. It forms fine needle-like crystals in its anhydrous state but clinorhombic crystals when it crystallizes with 1½ molecules of water.

Paraaminobenzene Sulphonic Acid, $C_6H_4\begin{cases}NH_2 & (1)\\ SO_3H & (4)\end{cases}$, is commonly known as sulphanilic acid, and it is formed when 1 part of aniline is heated with 3 parts of strong sulphuric acid to 180–190° C., or 100 parts of aniline sulphate may be heated on trays with 105 parts of strong sulphuric acid until on boiling a sample with caustic soda, the odor of aniline has disappeared.

The pure colorless crystals contain one molecule of water of crystallization which is lost on exposure to air, when the substance falls to a white powder. It dissolves slightly in water and it forms salts with bases because of its sulphonic acid group, and it forms salts with acids on account of its basic amino group.

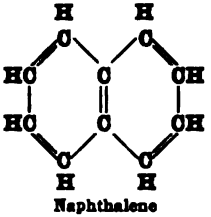
Aminotoluene Sulphonic Acids, $C_6H_3\begin{cases}CH_3\\ NH_2\\ SO_3H\end{cases}$. The ortho-toluidinemetasulphonic acid, $C_6H_3(CH_3 \cdot NH_2 \cdot SO_3H)$ (1.2.3) may be obtained by acting directly with concentrated sulphuric acid upon orthotoluidine $C_6H_4\begin{cases}CH_3 & (1)\\ NH_2 & (2)\end{cases}$, or by heating the sulphate of orthotoluidine to 200° C. If fuming sulphuric acid acts upon paratoluidine, two isomeric sulphonic acids result.

Xylidine Sulphonic Acids, $C_6H_2(CH_3)_2(NH_2)(SO_3H)$. Several isomers are possible with these four groups attached to a benzene ring; but the one technically important is the product from the treatment of ordinary commercial xylidine (alphaaminometaxylene) with concentrated sulphuric acid.

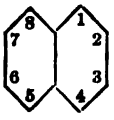
Benzidinesulphonic Acids. When hot fuming sulphuric acid is allowed to act on benzidine several different sulphonic acids result. If the temperature of 120° C. is not exceeded, then the principal product is a sulphone of benzidine, $C_6H_3NH_2$ | SO_2 | $C_6H_3NH_2$, which is converted by heating to 150–160° C.

into sulphonic acids of this sulphone; by a still higher temperature benzidine sulphonic acids result.

Sulphonic Acids of Naphthalene Derivatives



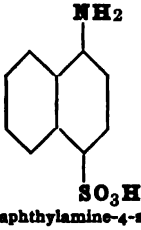
Naphthalene



Naphthalene. Condensed formula

The formula of naphthalene $C_{10}H_8$, is expressed so as to show its structure in the first figure above: the relative position of each of the ten carbon atoms and each of the eight hydrogen atoms. For the sake of simplicity the second figure is all that is needed to represent the formula of naphthalene when we are either considering any of its numerous derivatives or when it enters into the composition of a larger molecule.

When an amino derivative of naphthalene contains a sulpho acid group, it is at once identified by the numbers written in the name of the compound itself. For example, 1-naphthylamine-4-sulpho acid can indicate only the compound whose formula is shown below. (In this instance, the word amine forms a part of the name itself, and the number indicating its position stands in front of its name):



1-Naphthylamine-4-sulpho acid

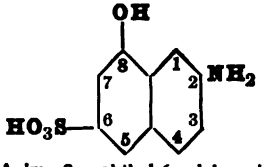
This same derivative of naphthalene is often called naphthionic acid.

Suppose a derivative of naphthalene contains an amino group, a hydroxyl group, and two sulpho groups. A very

large number of different derivatives of naphthalene may have these four groups substituting the hydrogen of naphthalene but no clue is given by this information as to which one is meant. If, however, the name of the substance is written so that the exact carbon atom to which the amino group is joined and also the carbon to which the hydroxyl is affixed and the carbon to which the two sulpho groups are joined; then the compound is at once separated and distinguished with precision from all its isomers.

If in this instance we find the substance named as 2-amino 8-naphthol-:6-sulpho acid, the position of each separate group which replaces a hydrogen in naphthalene is known definitely and it need not be confused with its isomers.

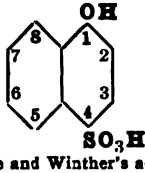
The compound must have the formula:



2-Animo-8-naphthol-6-sulpho acid (γ-acid)

This compound is also known under the name aminonaphthol-sulpho acid, γ or "γ-acid" for short.

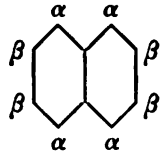
For purposes of speech the names employing numerals are clumsy and other names are given which attach the name or names of the discoverers to particular compounds. Capital letters form the briefest method of indicating a substance. One sulpho acid of naphthalene is known as Neville and Winther's acid: it is a 1-naphthol-4-sulpho acid. The hydroxyl (indicated by the syllable "ol" in the name) is attached to carbon No. 1 and the sulpho acid group to carbon No. 4. It must accordingly have the following constitution:



Neville and Winther's acid, or
1-naphthol-4-sulpho acid,
or aminonaphthol sulpho acid N. W.

Another method used in naming naphthalene derivatives refers to the positions α and β which the substituting groups take.

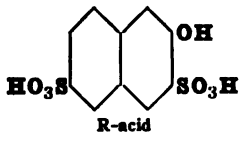
As the following figure indicates, there are four positions called alpha (α), and four called beta (β):



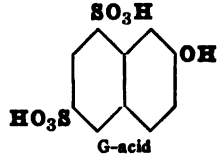
The acid of Neville and Winther above is according to this method called α-naphthol, α-mono-sulpho acid.

Since nearly two hundred derivatives of naphthalene are known which include naphthol, and naphthylamine sulpho acids, and dioxy, amidoxy, and diaminonaphthalene sulpho acids, the need of care and precision in distinguishing the separate compounds will be at once apparent.

Two β-naphtholdisulpho acids of great technical importance are known as R-acid and G-acid, and have the following structure: R (from roth, red) because this acid is used in making red dyes; G (from gelb, yellow) because this acid is used in making yellow dyes:



R-acid



G-acid

The **R-acid** is a 2-naphthol-3.6-disulpho acid and the G-acid is a 2-naphthol-6.8-disulpho acid. The methods of manufacture of these two acids will be given.

The patented method for making the R-acid consists in heating 1 part of β-naphthol, $C_{10}H_7OH$ with 3 parts of sulphuric acid at 100–110° for several hours. When the melted mass is dissolved in water to which common salt has been added, the sodium salt of R-acid, called **R-salt**, crystallizes out while the sodium salt of the G-acid, called G-salt, which is formed at the same time remains in solution.

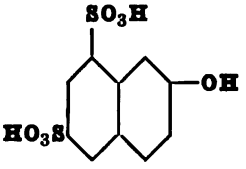
The method for preparing the G-acid most economically consists in using a larger amount of concentrated sulphuric

acid, but keeping the temperature much lower than for the R-acid and keeping up the process for a much longer time.

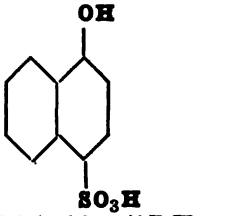
One part of β-naphthol is dissolved in 4 parts of concentrated sulphuric acid and kept at a temperature of 60° for 48 hours, or at a temperature of 20° for 8 to 10 days.

The **G-acid** is the principal product mixed with 10–15 per cent of the monosulpho acid S. This is removed by treating the alkaline solution with the requisite quantity of diazobenzene to combine with it, and the orange dye thus produced is filtered out of the solution of the G-acid. The salts of the G-acid dissolve more easily in water than those of the R-acid.

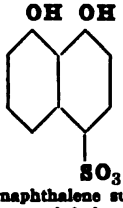
The most important amino and oxy, and amino-oxy derivatives of naphthalene used in the following pages of azo-dyes are given here with names and constitutional formulas.



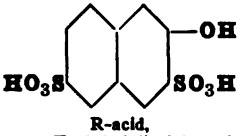
β-Naphthol disulpho acid,
or 2-naphthol-6-8-disulpho acid,
or G-acid



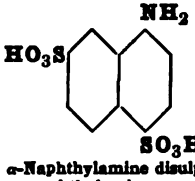
α-Naphthol sulpho acid N. W.
(Neville and Winther),
or 1-naphthol-4-sulpho acid,
or Neville and Winther's acid



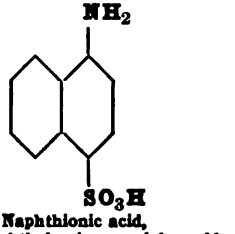
Dioxynaphthalene sulpho acid S,
or 1.8 dioxynaphthalene-4-sulpho acid



R-acid,
or β-Naphthol disulpho acid R.



α-Naphthylamine disulpho acid D,
or 1-naphthylamine-4-7-disulpho acid



Naphthionic acid,
or 1-naphthylamine-4-sulpho acid

The Phenols

Phenol or **Carbolic Acid.** If a single hydrogen atom of benzene is replaced by a hydroxyl group (—OH) the indifferent character of the benzene is so modified that it becomes acid in its nature. Common carbolic acid is such an acid whose formula is C_6H_5OH. The hydrogen joined to the oxygen is replaceable by metals and forms salts. The weak character of the acid is shown from the fact that carbonic acid is able to decompose the sodium salt.

Carbolic acid is also called phenol and the sodium salt sodium phenate or sodium carbolate, C_6H_5ONa. The acid nature of phenol is much strengthened by the entrance of negative atoms or groups of atoms into the benzene ring, e.g., trinitrophenol, $C_6H_2(NO_2)_3OH$, known as picric acid, is a much stronger acid than phenol.

Phenol is present in coal tar and it is recovered therefrom in large amounts. It may also be made from an alkali salt of benzene sulpho acid by fusion with a caustic alkali.

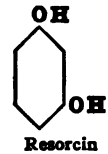
$$\underset{\substack{\text{Potassium}\\\text{benzene sulphonate}}}{C_6H_5SO_3K} + 2KOH = \underset{\substack{\text{Potassium}\\\text{phenate}}}{C_6H_5OK} + K_2SO_3 + H_2O,$$

$$C_6H_5OK + HCl = \underset{\text{Phenol}}{C_6H_5OH} + KCl$$

Under the name of carbolic acid, phenol has been employed in large quantities as an antiseptic. The acid consists of white crystals when pure in the form of long needles. These melt to a thick liquid by the addition of slight amounts of water at the ordinary temperature; then on adding a large quantity of water, the heavy syrup forms an oily layer under the water and slowly dissolves. Water at the ordinary temperature, however, will take up only 6 per cent of the acid.

Resorcin or **Resorcinol** is a substance which differs from phenol in possessing one more oxygen atom. It is therefore a dioxy- or a dihydroxybenzene. Of the three possible dihydroxybenzenes, resorcin is the one whose hydroxyl-

groups are in the positions 1 and 3, making it thus the meta hydroxybenzene, $C_6H_4(OH)_2$,



Resorcin

Resorcin is a white crystalline substance of a pleasant aromatic odor similar to phenol but not so strong. Like phenol it has antiseptic properties; but it is milder in its action. Large quantities are employed in the manufacture of the eosine dyes.

Among many methods of preparing resorcin, one is the fusion of the potassium salt of metabenzenedisulpho acid with caustic potash.

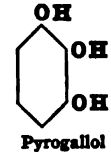
$$\underset{\text{Metabenzene-disulpho acid}}{C_6H_4(SO_3K)_2} + 4KOH = \underset{\text{Potassium resorcinate}}{C_6H_4(OK)_2} + 2K_2SO_3 + 2H_2O,$$

$$\underset{\text{Potassium resorcinate}}{C_6H_4(OK)_2} + 2HCl = \underset{\text{Resorcin}}{C_6H_4(OH)_2} + 2KCl$$

An aqueous solution of resorcin turns dark violet with ferric chloride and violet with chloride of lime. Exposure to the air turns the solution red.

Pyrogallol is the most important of the trihydroxy benzenes to which it belongs. There are three substances in this class, but pyrogallol is the one having all its hydroxyls in neighboring positions as seen below:

$C_6H_3(OH)1:2:3$



Pyrogallol

It crystallizes in white plates which melt at 132° and sublime unchanged.

One method of preparation is to heat gallic acid with three times its weight of glycerine to 190–200° until no more carbon dioxide is evolved.

$$\underset{\text{Gallic acid}}{C_6H_2(OH)_3COOH} + \text{heat} = \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + CO_2$$

Water dissolves pyrogallol easily and its solution rapidly absorbs oxygen from the air and turns dark in color.

The Naphthols

The Naphthols bear the same relation to naphthalene that the phenols bear to benzene. When the hydrogen atoms of naphthalene are replaced by hydroxyl groups, the naphthols are formed. As there are two kinds of hydrogen depending upon their position in the molecule, it follows that a single hydroxyl may produce two kinds of naphthol depending upon its point of fixation. These two substances are distinguished as α- and β-naphthol.

α-Naphthol is a solid substance which occurs in glistening needles. It is almost insoluble in cold water and only slightly soluble in hot; the sodium salt dissolves easily in a solution of sodium hydroxide, for the sodium salt is formed and this is easily soluble. α-Naphthol volatilizes with steam. A dark violet color is produced by chloride of lime. α-Naphthol is made by fusing α-naphthalene sulphonate of soda with two or three times its weight of sodium hydroxide and a small quantity of water at 270–300° in an iron vessel which is provided with a mechanical stirrer. The upper layer of sodium naphtholate is separated from the heavier layer of sodium hydroxide and sodium sulphite. After dissolving this in water, the decomposition of the salt takes place by using hydrochloric acid or even carbonic acid. Purification is accomplished by thorough drying and distillation.

β-Naphthol has a composition identical with α-naphthol. The difference is one of constitution: of the position of the single hydroxyl group which in this substance occupies the beta position. The method of preparation is similar to that

for α-naphthol except that the initial substance for the fusion with sodium hydroxide is β-naphthalene sulphonate of soda.

The difference in position of the hydroxyl group from that in the α-naphthol develops differences in its behavior; it is not volatile with steam nor does it show a coloration with ferric chloride or with chloride of lime.

β-Naphthol is white and crystallizes in plates which dissolve in alcohol and ether but sparingly in water. It melts at 123° and boils at 286°. The commercial product is nearly pure, but α-naphthol may be detected in so small an amount as .1–.5 per cent by dissolving it in alcohol, adding water and then a few drops of ferric chloride, when a violet color will appear.

The Aldehydes

Formic Aldehyde is used in the dye industry for condensing several benzene derivatives into larger molecules: furnishing, for example, the methane carbon atom so important as the ultimate nucleus of the triphenylmethane dyes. Its formula, CH_2O or HCHO, shows its simple composition and also that it differs from methyl alcohol, CH_4O, out of which it is made only by lack of two hydrogen atoms.

It is made by passing the vapors of methyl alcohol mixed with air over heated platinum charcoal or coke, thus two hydrogens are oxidized away, producing the formic aldehyde. At the ordinary temperature, it is a gas which condenses to a liquid only at −21° C. It condenses readily enough by dissolving in water and an aqueous solution containing 40 per cent of the aldehyde is the usual strength of the commercial aqueous solution. Formaldehyde is one of the safest and best antiseptics known.

Benzaldehyde may be regarded as formic aldehyde, HCHO, in which one of the hydrogens has been replaced by the phenyl-group —C_6H_5, so as to form C_6H_5CHO. It is, however, industrially prepared from toluene or methylbenzene, $C_6H_5CH_3$, which requires that the methyl (—CH_3) group be transformed into the aldehyde group. This cannot be done directly. The toluene is first chlorinated by passing

chlorine gas into boiling toluene, producing thereby benzyl chloride or benzal chloride, which on treatment with water and lead nitrate in the first instance and with lime and water in the second yield benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \rightarrow \left.\begin{matrix} C_6H_5CH_2Cl \\ C_6H_5CHCl_2 \end{matrix}\right\} \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

Benzyl chloride
Benzal chloride

Benzaldehyde is a pleasant-smelling liquid used in flavoring cakes and confections. It boils at 129° and dissolves easily in alcohol but only slightly in water. Oxidation even by the air converts it into benzoic acid. It is employed in the dye manufacture for a purpose similar to that of formaldehyde, i.e., to condense benzene derivatives and furnish the methane carbon as a nucleus for the developed dyes.

CHAPTER V

THE NITRO AND NITROSO DYES

The Nitro Dyes

The activity of nitric acid is so great and its reactions are so characteristic that it might be expected that the results and products of its action would early excite attention in the domain of color research.

It is so destructive of animal tissues, the yellow stains which betray contact with it so irremediable, that the disintegration would appear to be complete. In many instances, however, when an organic compound is apparently destroyed, the disintegration has proceeded only a certain and definite portion of the way toward complete dissolution of the substance. At the point of arrested action, a new chemical individual has been formed which the acid then ceases to attack.

These new products have been investigated, their valuable properties ascertained and put to the service of the manufacture of both dyes and explosives.

Picric Acid. This yellow dye was discovered more than a century ago, in 1771, by Woulfe, who obtained a liquid that would dye silk yellow by allowing nitric acid to act upon indigo.

Since that time, it has been rediscovered by many different investigators and it has been obtained from substances as unlike as indigo, silk, wool, carbolic acid and a resin (acaroid resin—yellow gum of Botany Bay), by the chemical action upon these of nitric acid.

It was Welter who in 1799 found that picric acid was formed when nitric acid acted on silk. He, however, did not

know that his product was the same as that obtained by Woulfe and it was called Welter's bitter.

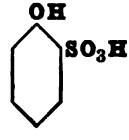
Liebig proved that indigo bitter and Welter's bitter were one and the same substance. He named it " kohlenstickstoff-saure " or carbazotic acid. Berzelius called it " pikrinsalt-petersaure." Dumas analyzed the yellow compound and gave the dye its present name picric (from πικρος, bitter) acid. Laurent, in 1842, found that it could be made from phenol or carbolic acid and still later in 1869 that it could also be made and more easily, from phenol sulphonic acid.

Picric acid is the final oxidation product of many aromatic substances; as oxalic acid is the final product of oxidation of many fatty compounds. Its production from silk, wool, indigo, resin, and carbolic acid shows that the benzene ring is present in them all. (Some doubt, however, has been expressed that it is obtained from wool.)

Picric acid may be made direct from phenol by the action of strong nitric acid, but the action is violent and the product less satisfactory than when the manufacture proceeds in two steps. At present, the phenol is first changed into phenol sulphonic acid, $C_6H_4SO_3H(OH)$, by allowing it to run into and dissolve in concentrated sulphuric acid: what takes place is shown in the reaction,

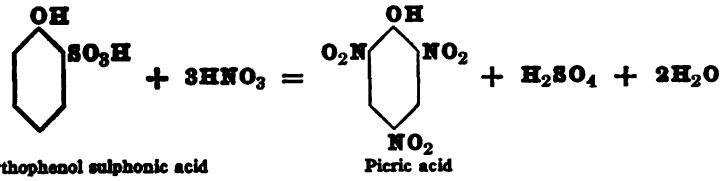
$$C_6H_5OH + H_2SO_4 = C_6H_4(OH)SO_3H + H_2O$$

Both the ortho and the para phenolsulphonic acids are formed by this procedure; but at a moderate temperature the former is the more abundant, while at the temperature of boiling water the latter is more largely formed. On heating the ortho product, it is transformed into the para product, but both varieties are converted into picric acid when strong nitric acid is allowed to work upon them as shown below:



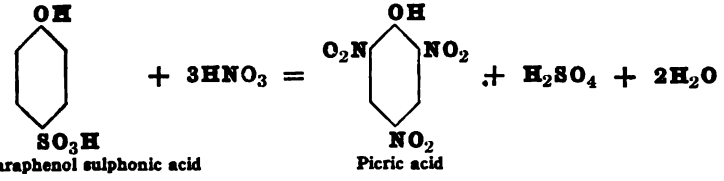
Orthophenol sulphonic acid

Paraphenol sulphonic acid



Orthophenol sulphonic acid — Picric acid

also



Paraphenol sulphonic acid — Picric acid

In the phenolsulphonic acid, the sulpho group ($—SO_3H$) is replaced by a nitro ($—NO_2$) group. Two hydrogen atoms are also replaced by nitro groups, making the product a trinitro compound. These three nitro groups always take up positions that are symmetrically situated, e.g., representing phenol with its hydroxyl in position 1, the nitro groups attach themselves in positions 2:4:6.

The influence of the entrance of these three nitro groups is seen in this: that phenol itself, though an acid, is too weak to decompose the carbonates, while, after the nitro groups have entered, the resulting picric acid does decompose the carbonates.

Picric acid occurs in pale yellow lustrous crystalline scales or in rhombic prisms, depending upon whether it was crystallized from water or alcohol or from ether. It is but sparingly soluble in cold water; more easily soluble in hot water. Alcohol, ether, and benzene likewise dissolve it. The solutions color the skin and animal fibers a pure yellow.

The taste is intensely bitter and it has been said that picric acid was once used to give a bitter taste to beer. Twelve milligrams of the acid in a liter of beer impart to it an unbearable bitter taste.

Picric acid is poisonous. Doses from .06 to .6 gram have proved fatal to rabbits and dogs.

Wool, silk, and leather have been dyed a pure yellow.

The coloring power is very great. It has also been used to combine with reds and blues for dyeing shades of orange and gray.

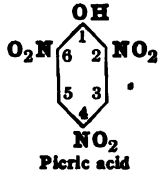
The explosive character of its salts has caused it to be used in the manufacture of high explosives, and it is now far more largely employed in this industry than for dyeing, wherein it has been superseded by the later yellow dyes.

Picric acid unites with benzene and other aromatic hydrocarbons to form crystalline compounds, which on occasion may serve alike for the identification of picric acid or the hydrocarbons with which it combines. With naphthalene there is formed a very characteristic compound, $C_{10}H_8+C_6H_2(NO_2)_3OH$, which crystallizes in golden scales, melting at 149°.

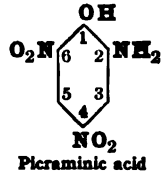
Picraminic Acid. When picric acid is subjected to the action of reducing agents, the nascent hydrogen will gradually remove the oxygen atoms from all the three nitro groups and replace them with hydrogen atoms, thus converting all the nitro ($—NO_2$) groups into amino ($—NH_2$) groups. This reducing action may be limited to the conversion of a single one of the nitro groups into an amino group by employing the comparatively weak reducing agents, hydrogen sulphide and ammonia. This partial reduction product is picraminic acid.

$$C_6H_2(NO_2)_3OH + 6H = C_6H_2(NO_2)_2(NH_2)OH + 2H_2O$$

The structure may be compared with the original picric acid as follows:



Picric acid



Picraminic acid

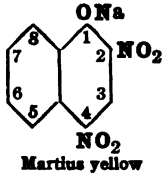
Picraminic acid has become an important substance in the manufacture of the azo dyes.

Martius yellow, 1864, has the distinction of being the first very beautiful yellow obtained by the synthetic processes. This yellow dye may be prepared in several ways, but the

simplest to understand is the action of nitric acid upon α-naphthol. What takes place is the fixation of two nitro-groups in positions 2 and 6 of the α-naphthol.

$$\underset{\alpha\text{-Naphthol}}{C_{10}H_7OH} + 2HNO_3 = \underset{\text{Martius yellow (free acid)}}{C_{10}H_5(NO_2)_2OH} + 2H_2O$$

The dye itself is the sodium salt, sometimes the potassium salt of this acid, and possesses the following constitution:



Martius yellow

Martius yellow is an orange yellow powder as it appears in commerce. When heated, the sodium salt deflagrates suddenly while the ammonium salt burns quietly. The sodium salt requires 35 parts of water for solution; but 265 parts are needed for the corresponding amount of the calcium salt.

By adding hydrochloric acid to the aqueous solution, the free dinitronaphthol falls as a precipitate. In strong sulphuric acid, a yellow solution is formed which on diluting with water lets fall a yellow precipitate.

Wool in acid bath is dyed a beautiful golden yellow while silk is colored the same shade in a soap bath or in "boiled-off liquor." Varnishes are often tinted with this dye. The absence of any bitter taste which is characteristic of the nitro dyes has caused it to be used in coloring food products, e.g., noodles and macaroni; but its known poisonous nature renders the practice unsafe.

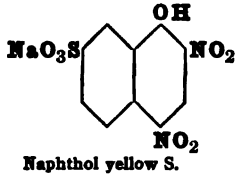
Naphthol yellow S. differs from Martius yellow just considered only in possessing a sulphonic acid ($-SO_3H$) in position 7 in the molecule. It is, however, not prepared by implanting a sulphonic acid group in this dye. A trisulphonic acid of α-naphthol is used instead as the starting point. This substance is treated with nitric acid, whereby two of the sulpho groups are replaced with nitro groups:

$C_{10}H_4(SO_3H)_3OH + 2HNO_3 =$

α-Naphthol trisulpho acid 2:4:7

$C_{10}H_4(NO_2)_2(SO_3H)OH + 2H_2SO_4$

Naphthol yellow S



Naphthol yellow S.

Naphthol yellow S is a bright yellow or orange powder which burns with bright yellow scintillations. On account of the sulpho group, which this possesses over Martius yellow, it is a more valuable dye. It is more soluble and acids cause no precipitate in its yellow solution.

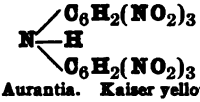
A marked difference is shown in the behavior of this dye toward sodium and potassium hydroxide; for the first has no apparent effect, while the second causes a yellow flocculent precipitate to form in the most dilute solutions.

Wool and silk are dyed yellow from an acid bath, and, since it is the most valuable of the nitro dyes, it is sometimes adulterated by the admixture of Martius yellow.

Aurantia: Kaiser yellow, 1873, is a dye which produces a fine orange color upon fabrics; but its use is prohibited because of eruptions which it excites on the skin. It is employed in photography as a light screen.

The action of nitric acid upon diphenylamine causes the fixation of six nitro groups in the molecule of the latter as shown below; the result being aurantia.

Diphenylamine

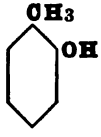


Aurantia. Kaiser yellow

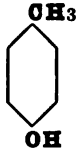
Victoria orange is an almost obsolete dye which was formerly used to color liqueurs, macaroni, etc., until its poisonous properties were known.

The firm of Fr. Baeyer & Co. have placed one form of this dye (dinitro orthocresol) on the market under the name of antinonnin. This is employed to kill fungus growths upon masonry and wood in moist places.

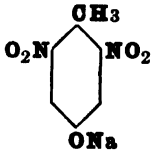
Victoria orange is a mixture of the sodium salts of ortho and paradinitro cresol, and it may be prepared by allowing strong nitric acid to act on cresol sulphonic acid.



Orthocresol



Paracresol

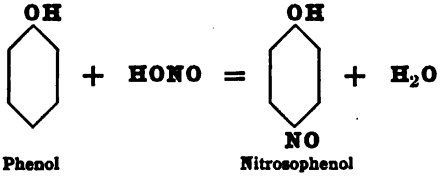


Paradinitro cresol sodium salt: one form of Victoria orange

The Nitroso Dyes, or Quinoneoximes

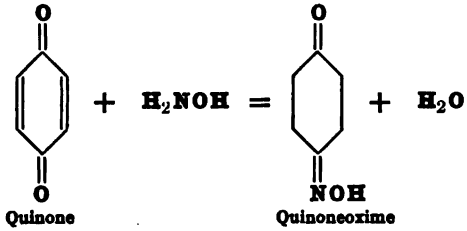
Nitrous acid acts readily upon bodies which possess the properties of phenol or carbolic acid, and in doing so it converts these white substances into new ones. These new products by the aid of salts of iron and salts of chromium produce valuable green dyes.

There has been some change in the way this chemical action has been regarded, and, before considering an actual nitroso dye, we may consider the action of nitrous acid upon simple phenol. This action may be represented as follows:



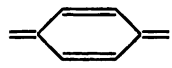
Phenol — Nitrosophenol

If hydroxylamine (H_2NOH), is allowed to act upon quinone, the same so-called nitrosophenol is formed as shown below:



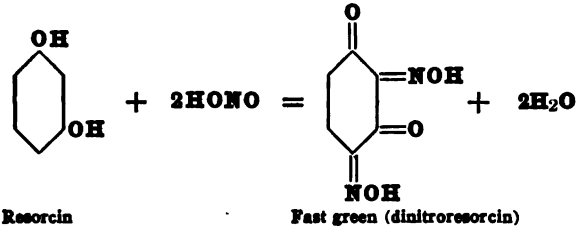
Quinone — Quinoneoxime

The formula of quinoneoxime is regarded as the more probable one for the product of nitrous acid when it acts upon phenol: at least this product behaves as a quinoneoxime behaves in many reactions. Two definite reasons may be given for choosing the latter formula: first, the nitroso phenol has a very feeble acid character which accords better with the quinoneoxime structure: second, the power to form a dye is believed to belong especially to the quinone ring,



and the oxime structure contains such a ring.

Fast green, 1875; Solid green O.; and Resorcine green, are names for the same dye. It is prepared by the action of nitrous acid on resorcin. The latter substance is white and crystalline and it easily dissolves in water. By adding sodium nitrite and the corresponding amount of sulphuric acid to the aqueous solution, nitrous acid is formed and begins at once to work upon the resorcin, changing it into dinitroresorcin of the following composition:



Resorcin Fast green (dinitroresorcin)

Fast green appears either as a dark green paste or as a grayish brown powder which is slightly soluble in cold; but more easily in boiling water.

For dyeing, fast green requires the aid of an iron salt as a mordant. Cotton mordanted with iron is dyed a green which is moderately fast to the action of both light and soap. Wool thus mordanted is dyed a green which is very fast to light.

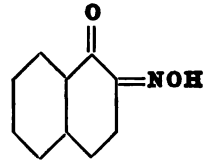
Fast green by reason of its acid properties has the power to combine with the basic dyes. Use is made of this property by treating cotton cloth with the fast green dissolved in a solution of ammonia, caustic soda, or sodium acetate.

This produces a beautiful brown color that is fast, and this brown shade may be modified in various ways by afterward treating it with a basic dye.

Gambine R. is the product formed by the action of nitrous acid upon a substance of phenolic character called α-naphthol. A greenish yellow paste appears when the process is finished which dissolves with some difficulty in water, coloring it yellow. The reaction involves one molecule of nitrous acid and one molecule of α-naphthol.

$$\underset{\alpha\text{-Naphthol}}{C_{10}H_7OH} + HONO = \underset{\text{Gambine R.}}{C_{10}H_6(O)NOH} + H_2O$$

The oxime group (—NOH) derived from the nitrous acid takes an ortho position in respect to the quinone oxygen:

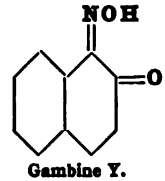


Gambine R.
α-Naphthoquinoneoxime

Hydrochloric acid does not affect it while sodium hydroxide forms a clear yellow solution. A reddish brown solution is formed with strong sulphuric acid; but this turns yellow on adding water when brownish flocks also separate.

Fabrics mordanted with a ferrous salt are dyed an olive green; but if a chromium mordant is used, the resulting color is brown. These colors are fast to light and washing.

Gambine Y. Under this name, there appears in the trade an olive green paste. Like **gambine R.** above, it is formed when nitrous acid is allowed to act upon a naphthol. It is, however, β-naphthol which is employed in place of α-naphthol. The constitution seen below shows the positions of the oxime and the quinone oxygen to be just reversed from those of gambine R.



Gambine Y.

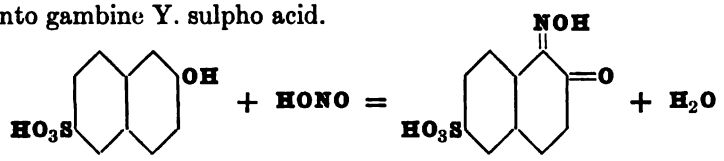
These two dyes are therefore isomers, and the influence of change of position in the shade of the color may be seen; for **gambine Y.** dyes a pure green, while **gambine R.** dyes an olive green.

Gambine Y. dyes goods mordanted with ferrous salts green.

Naphthol Green B. is a nitroso dye which, unlike the other members of this class, does not require a mordant upon the fabric to be dyed. The reason for this is that the dye is already united to the mordanting substance before being applied to the fiber. This combination of dye and mordant known as **naphthol green B.** would be insoluble and therefore impossible of application as a dye were it not made soluble by treatment with sulphuric acid. This transforms it into a soluble sulphonic acid whose sodium salt is the commercial form of the dye.

By observing the formula below, it will be noticed that it resembles perfectly gambine Y. with a sulpho group (—SO_3H), in the position 6 of the naphthalene ring and with the further modification of having the two sulphonated groups of **gambine Y.** combined with an atom of iron.

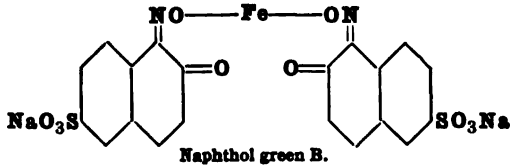
The manufacture of this dye is a good instance of an indirect method. Gambine Y. is not first made, then sulphonated and then combined with iron. Instead of this procedure, Shaeffer's β-acid, which is β-naphthol containing a sulpho group in position 6, is used as the starting point. Nitrous acid converts this into gambine Y. sulpho acid.



Schaeffer's acid. β-Naphtholmonosulpho acid

Gambine Y. Sulpho acid

Treatment of this latter substance with a ferrous salt causes a union of two of these groups with an atom of iron.



Naphthol green B.

This complex compound will dissolve in water and is suitable for dyeing. Naphthol green B. is a dark green powder which dissolves in water with a dark green color; but on standing this aqueous solution decomposes. If it is heated on platinum foil, a residue of sulphide of iron remains behind.

When warmed with hydrochloric acid, it changes to yellow. Sodium hydroxide turns it a bluish green. The solution in strong sulphuric acid is yellow-brown, but on dilution with water it changes to yellow.

Wool from an acid bath is dyed a green which is fast to light and the effects of milling. It further resists the action of acids and alkalies.

CHAPTER VI

THE TRIPHENYLMETHANE DYES

THE dyes of this class were among the earliest to command attention in commerce. Many beautiful and valuable shades of red, violet, blue, and green are found among them. It is a little more than a half century since the first one was discovered, and they still maintain an honorable place among their rivals. These dyes attained a technical importance long before the chemistry of their manufacture was understood. The empirical processes at first employed gave but meagre yields and therefore increased the cost. As will be shown later persistent research finally rendered the chemistry of the methods intelligible, increased the yields and diminished the cost to an extraordinary degree.

On studying the constitution of these dyes, a common nucleus appears in the formulas of them all, and it has very properly given its name to the class. This nucleus is **triphenylmethane**; or so much of it as remains unsubstituted by those other groups of atoms or radicals which are required to develop from it the various shades of the individual colors.

Triphenylmethane may be considered as methane in which three hydrogen atoms have been replaced by three phenyl ($—C_6H_5$) groups. In appearance, it is a white substance which crystallizes in beautiful prisms that melt at 93° and boil at 359°. Neither cold water nor cold alcohol will dissolve it; but it is readily soluble in hot alcohol, ether, or benzene. On crystallizing from its solution in benzene, it has the power of retaining one molecule of "benzene of crystallization."

Triphenylmethane may be prepared synthetically in a variety of ways; but the one employing chloroform and benzene is easy to understand. When these substances

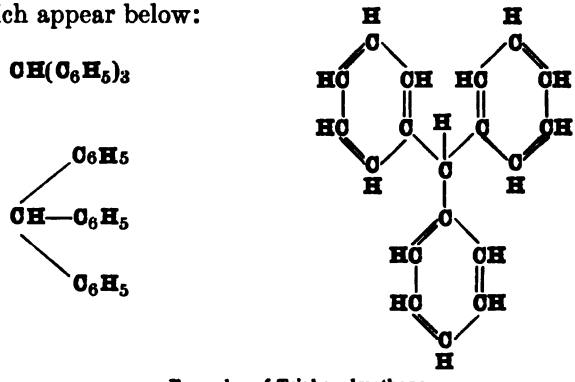
are brought together in the presence of aluminum chloride, the following reaction takes place:

$$\underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Benzene}}{3C_6H_6} = \underset{\text{Triphenylmethane}}{CH(C_6H_5)_3} + 3HCl$$

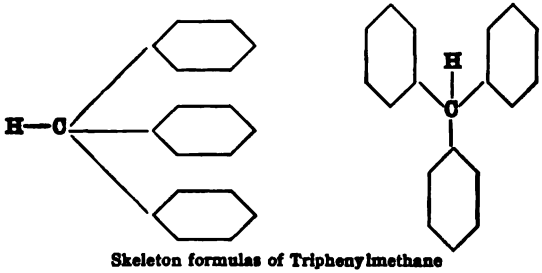
The aluminum chloride causes the action, but it forms no part of the product.

Though it is possible to start with triphenylmethane in making dyes of this class and though it has actually been accomplished in a particular instance, as will be shown later, yet in the manufacture itself this is never done. In fact many of these dyes were made a score of years before it was proved that the triphenylmethane nucleus was present in any one of them.

The commercial processes are simplified by starting with derivatives of benzene and causing these to unite, as will be seen in numerous instances in the following pages. The formula of triphenylmethane is written in many ways, several of which appear below:



Formulas of Triphenylmethane



Skeleton formulas of Triphenylmethane

The Triphenylmethane Dyes

Rosaniline, Fuchsine, Magenta. A variety of this brilliant red dye is thought to have been discovered by Natanson in 1856, the same year in which the English Chemist W. H. Perkin discovered the famous mauve. The manufacture of this substance was carried on by various firms, for different methods of making the same dye were soon discovered. It attained an even more brilliant success than Perkin's mauve. Millions of dollars were invested in its production. A great monopoly arose in France and the dyestuff sold at one time for as much as one hundred dollars per pound. For half a century it has maintained a place among its rivals.

Two chief processes have been employed in its production—one, the arsenic process, the other, the nitrobenzene process. The former is the older and until later years was used almost exclusively, but unfortunately the product contained arsenic acid, at times as high as 6 per cent; the latter method has the great advantage of giving a purer product and one that is entirely free from arsenic.

Rosaniline appears in commerce under different names, some sentimental, some derived from its source. Magenta, for instance, was applied to it because of the victory of the French over the Italians at Magenta in 1859. A French chemist, Professor Verguin, in the employ of the Renard Bros., who discovered it in 1859, named it fuchsine from "fuchs—fox" the equivalent of his firm's name in German. Rosaniline was given to it on account of its source—aniline, and its rose-red color.

Commercial rosaniline in the form of the hydrochloride appears in crystals of a brilliant greenish bronze luster; the sulphate is a crystalline powder with greenish luster. The acetate forms irregular lumps with similar luster.

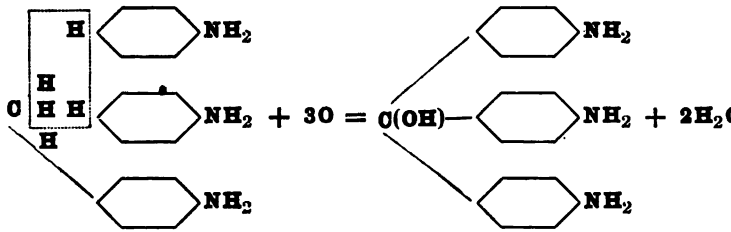
The dye is soluble in water, alcohol and amyl alcohol, with a red color. Ether does not dissolve it.

Hydrochloric acid turns the red aqueous solution yellow, while sodium hydroxide renders it colorless and causes the color base to settle to the bottom.

Strong sulphuric acid dissolves the dye to form a yellowish brown solution: addition of water turns it almost colorless. Wool, silk and paper are dyed a rosaniline red. Cotton is dyed the same shade after it has been first mordanted with tannin and tartar emetic.

Commercial rosaniline is not a single individual substance. It consists of a mixture of the salts of two substances, pararosaniline and rosaniline. These compounds of themselves have no color and they can only become dyes on combining with acids to form salts. They are oxygen derivatives of triaminotriphenylmethane and triaminodiphenyltolylmethane. These derivatives contain but one oxygen atom each in the large and complex molecules. This single oxygen atom in each case is joined to the methane carbon and owing to this fact the compounds are known as carbinols.

Pararosaniline will be considered first and then the structure and deportment of rosaniline itself will be clearly understood. Pararosaniline is made by the oxidation of a mixture of aniline $C_6H_5NH_2$ and paratoluidine $C_6H_4(CH_3)NH_2$. It is from the name of this latter substance that the para of pararosaniline is derived. Various oxidizing agents have been used; but those chiefly employed have been arsenic acid and nitrobenzene. Two molecules of aniline and one of paratoluidine are thus joined as indicated in the reaction:



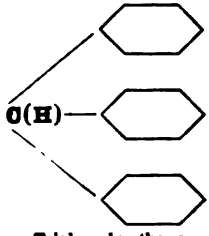
2 mols. aniline
1 mol. paratoluidine

Pararosaniline base.
Triaminotriphenyl carbinol.
A colorless crystalline solid

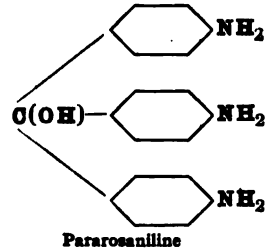
The carbon atom of the methyl group in paratoluidine is the one which loses hydrogen, thus leaving its valences free to unite with the other molecules from which oxidation has

also removed hydrogen. It will be noted also that one oxygen atom has found lodgment between the methane carbon and its only remaining hydrogen atom. This single atom of carbon is called the methane carbon, since it is the nucleus of the molecule and because the whole complex molecule may be regarded as a molecule of methane in which the four hydrogen atoms have been replaced by the larger groups of atoms now attached to it.

Study of this formula shows that a nucleus of triphenylmethane is present and that the three amino groups are distributed one to each benzene ring or phenyl group as shown in the formula below:



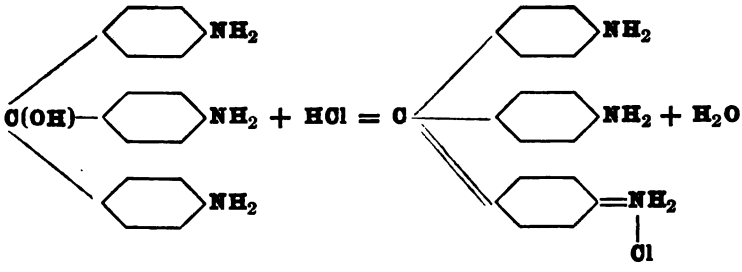
Triphenylmethane



Pararosaniline (colorless)

The function of the methane carbon atom is here clearly shown and the three amino groups are not only affixed to separate benzene rings, but they occupy similar positions, and these are all upon the extreme ends of the benzene rings opposite to that where the attachment to the methane carbon occurs. It is definitely known that these are the true relative positions of the amino groups. The proof of this is given later.

The true dyestuff is formed from this colorless base by the action of an acid. The acid combines to form a salt with the elimination of water, and the salt thus produced is the dyestuff itself. Many different theories have been maintained about the structure of the molecule which results from the separation of water and the formation of the salt which is the dyestuff; but the following reaction exhibits the structure now chiefly ascribed to pararosaniline.



Pararosaniline (colorless) — Pararosaniline hydrochloride. The red dyestuff

Proof of the Relation of Rosaniline to Triphenylmethane

Although rosaniline was discovered in 1856, and although the brilliancy of the dye and the high price it commanded attracted large amounts of capital to its manufacture and furthermore excited great rivalry among chemists in producing the dye by new methods not covered by patents, still its structure was not understood until more than twenty years later.

A. W. Hoffman in 1861 began the scientific study of rosaniline, and he came to the mistaken conclusion that the nitrogen atoms of the aniline formed the nucleus of the dye molecule. In 1867 Kekulé contributed the idea that the $—CH_3$ group of the toluidine played the part of a nucleus and held the complex parts together. Zulkowski, in 1869, made the assumption that there were three $—NH_2$ groups in the molecule and that it was a derivative of a hydrocarbon, $C_{18}H_{14}$. A number of other investigators worked upon the problem until in 1878 Emil and Otto Fischer succeeded in converting pararosaniline into triphenylmethane and rosaniline into diphenyltolyl methane. This work solved the problem.

The character of the proof used by E. and O. Fischer showing that pararosaniline was a derivative of the hydrocarbon triphenylmethane is given below.

They first proved that leucaniline was a primary triamine, for, on treatment with nitrous acid and subsequently boiling

the product with absolute alcohol, they actually obtained triphenylmethane according to the following reactions.

$$HC(C_6H_4NH_2\cdot HCl)_3 + 3HNO_2 = HC(C_6H_4N{=}N{-}Cl)_3 + 6H_2O$$

Paraleucaniline. Triaminotriphenylmethane — Diazo compound of triaminotriphenylmethane

$$HC(C_6H_4N{=}N{-}Cl)_3 + 3C_2H_6O = HC(C_6H_5)_3 + 3N_2 + 3HCl + 3C_2H_4O$$

Alcohol — Triphenylmethane — Aldehyde

Thus in two operations all the nitrogens were eliminated and the hydrocarbon triphenylmethane stood revealed as the foundation of this class of dyes.

But these investigators did not rest here: they wished to reconvert this triphenylmethane back into the paraleucaniline and this into pararosaniline. Their labors toward this end were successful, and the following reactions exhibit their method.

Triphenylmethane on treating with nitric acid is changed into a trinitrotriphenylmethane:

$$HC(C_6H_5)_3 + 3HNO_3 = HC(C_6H_4NO_2)_3 + 3H_2O$$

Triphenylmethane — Trinitrotriphenylmethane

By reduction with nascent hydrogen this latter product is converted into triaminotriphenylmethane:

$$HC(C_6H_4NO_2)_3 + 18H = HC(C_6H_4NH_2)_3 + 6H_2O$$

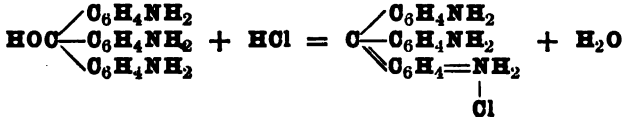
Paraleucaniline (colorless). Triaminotriphenylmethane

By oxidation this changes as follows:

$$HC(C_6H_4NH_2)_3 + O = HOC(C_6H_4NH_2)_3$$

Pararosaniline (colorless). Triaminotriphenyl carbinol

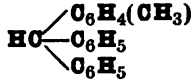
By the action of hydrochloric acid a salt is at once formed, the color of the true dyestuff is developed in accordance with the following reaction:



Pararosaniline.
(The commercial dye)

Careful study of these transformations and those that follow will be most thoroughly repaid, for an understanding of them will enable the student to comprehend this entire class of triphenylmethane dyes.

By an exactly similar method, E. and O. Fischer showed rosaniline was a simple homologue of pararosaniline, in fact, a methylpararosaniline, and was convertible into diphenyltolylmethane:

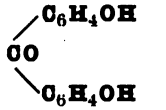


Diphenyltolylmethane

Position of the Amino Groups in Pararosaniline

In the preceding work, which demonstrated that the triphenylmethane was the hydrocarbon nucleus of pararosaniline, nothing was said about the position of the $-NH_2$ groups in the pararosaniline. We have to bear in mind that the use of the syllable para in the same pararosaniline was not given to it to suggest structure, only to indicate the use of paratoluidine in its manufacture. The elucidation of the real position of $-NH_2$ groups depends upon the consideration of the following facts.

First. Pararosaniline on being heated with water breaks up with the formation of diparadioxybenzophenone:



Diparadioxybenzophenone

In this compound the two hydroxyl groups occupy the positions of two of the $—NH_2$ groups of the pararosaniline, and as these hydroxyls are known to be in a para position to the methane carbon of this compound, the $—NH_2$ groups must likewise have been in the para position in the pararosaniline whence it came. This proves, so far, that at least two $—NH_2$ groups out of the three have the para position, but nothing in regard to the third. To prove the position of the third involves a somewhat indirect but still conclusive line of reasoning.

Second. By acting upon benzaldehyde with two molecules of aniline, there is produced diaminotriphenylmethane shown here:

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + 2\underset{\text{Aniline}}{C_6H_5NH_2} = \underset{\text{Diaminotriphenylmethane}}{CH(C_6H_4NH_2)_2(C_6H_5)} + H_2O$$

By heating with water and fusing with caustic potash this diaminotriphenylmethane is converted into diparaoxybenzophenone by the reaction indicated below:

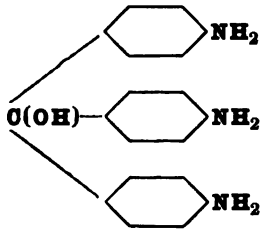
$$\underset{\substack{\text{Diaminotriphenyl-}\\\text{methane}}}{CH(C_6H_4NH_2)_2(C_6H_5)} \rightarrow \underset{\substack{\text{Dioxytriphenyl-}\\\text{methane}}}{CH(C_6H_4OH)_2(C_6H_5)} \rightarrow \underset{\substack{\text{Paradioxybenzo-}\\\text{phenone}}}{CO(C_6H_4OH)_2}$$

In this compound the two hydroxyl (—OH) groups are known to be in the para position to the methane carbon, and therefore the two amino ($—NH_2$) groups which were replaced by the hydroxyl (—OH) groups must have occupied the para position in the original diaminotriphenylmethane.

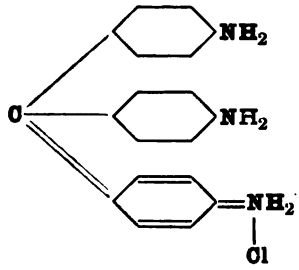
Third. If for the condensation with aniline, we select in place of benzaldehyde, paranitrobenzaldehyde, then according to the following reaction there results paranitrodiaminotriphenylmethane. By reduction this is converted into paratriaminotriphenylmethane.

We may now be sure that the third amino ($—HN_2$) group in triaminotriphenylmethane occupies a para position, because it was already in the para position as a nitro group in the paranitrobenzaldehyde employed for the reaction. Thus

all three amino (NH_2) groups hold para positions in reference to the methane carbon. The triaminotriphenylmethane is easily oxidized to pararosaniline, whose formula may now with certainty be written as follows:



Pararosaniline (colorless).
Triaminotriphenyl carbinol



Pararosaniline (the dye)

We are now in the position to appreciate the perplexity of the early investigators who, after preparing an aniline of especial purity, were unable on oxidation of it to obtain any rosaniline at all. Pure aniline contains no methyl-group to furnish the necessary methane carbon atom as nucleus of the dye molecule. The ordinary commercial aniline always contained toluidine, and it was the methyl (—CH_3) group of the toluidine which all unknown to the earlier chemists furnished this needed methane carbon for a nucleus.

Manufacture of Rosaniline

Arsenic Acid Method. Aniline oil for red containing, as found in commerce, both ortho- and paratoluidine is poured into an iron kettle. For each 100 parts of aniline, 125 parts of 75 per cent syrupy arsenic acid are added. The covered kettle is provided with a distilling tube through which during the eight hours' boiling, a considerable portion of a mixture of aniline and water, called "échappes" (from *échapper*, to escape), distills over and is saved. The temperature is maintained somewhat above the boiling point of aniline and by means of a rotating stirrer within the kettle the mass is kept in constant agitation.

The residue in the kettle is then boiled with water which dissolves the dye in the form of arseniate and arsenite of

rosaniline: some chrysaniline, excess of arsenic acid and resinous substances also go into solution.

The insoluble residue contains manvaniline, violaniline and chrysaniline.

The filtered solution of the dye and its soluble impurities is treated with a large excess of common salt. The arseniate of rosaniline is decomposed by the salt forming hydrochloride of rosaniline and sodium arseniate. The strong salt brine from the excess of salt causes the coloring matter to separate out. This use of a solution of salt to precipitate a dye is called "salting out." It is of very frequent use in the dye industry.

The precipitated rosaniline is crystallized from water, and it may be redissolved, salted out again, and recrystallized. The mother liquors contain an impure rosaniline and they are worked up for inferior grades (chrysaniline, cerise, geranium, etc.). The yield of rosaniline is about 25–42 per cent of the amount demanded by the theory.

The Nitrobenzene Process. The previous process always gave a poisonous product on account of the arsenic which was retained: sometimes as high as 6 per cent in crude manufacture. To obviate this disadvantage nitrobenzene and ferrous chloride were made to replace the arsenic acid as an oxidizing agent. The ferrous chloride with hydrochloric acid is oxidized by the nitrobenzene to ferric chloride and this then oxidizes the aniline, the nitrobenzene not entering into the formation of the dye. To 100 parts of aniline oil, two-thirds of the quantity of hydrochloric acid necessary for saturation is added and then 50 parts of nitrobenzene. The mixture is heated and agitated: meanwhile, 3 to 5 parts of iron filings are gradually added. The separation of rosaniline is accomplished as in the arsenic process. Considerable induline results as a by-product, but no chrysaniline. A much purer rosaniline is produced by this process and one entirely free from arsenic. This method is now almost exclusively used.

Formaldehyde Process. Formaldehyde has been used to furnish the methane carbon of rosaniline. It forms with aniline an anhydroformaldehydeaniline which when treated

with more aniline forms a rosaniline. The method is capable of easy production of substituted rosaniline, by taking substituted anilines for the starting point.

Constitution of Pararosaniline Hydrochloride

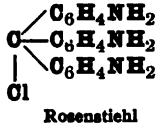
Three constitutional formulas among others for the dye pararosaniline hydrochloride have been proposed, which have had their stout defenders.

1. The one proposed, and stoutly maintained by Rosenstiehl, exhibits the chlorine attached directly to the methane carbon atom.

2. That proposed by E. and O. Fischer has the chlorine atom attached to the nitrogen and the valence which in Rosenstiehl's formula holds the chlorine is also attached to the nitrogen, recalling the older formula of quinone.

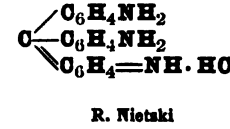
3. Nietski's formula resembles Fischer's so far as the position of the chlorine, but the fourth valence of the methane carbon is attached to the nearer end of the benzol ring, carrying the nitrogen and causing a readjustment of the valences in the ring itself so that nitrogen is also held to the ring by two valences.

This arrangement, in accordance with Fittig's quinone formula, is called the " quinoid " linking. The latter formula is now largely given the preference. The following formulas clearly exhibit their several differences:



Rosenstiehl

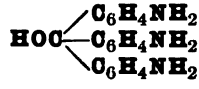
E. & O. Fischer



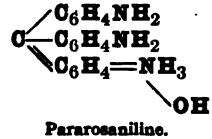
R. Nietski

Constitution of Pararosaniline

Considerable proof has accumulated to show that the pararosaniline, which has long been regarded as a carbinol of the following type.



has an isomer in the form of an ammonium base with the hydroxyl, not joined to the methane carbon, but to a nitrogen atom, thus forming a true ammonium base as shown below:



Pararosaniline.
(Ammonium base)

Hantsch maintains that the dyes are really salts of this ammonium base and not of the carbinol base, and that the carbinol base is transformed into the ammonium base before it can combine with an acid, eliminating water, to form a salt and develop the properties of a dye. This would make the rearrangement of valences to form the quinoid linking a function of the color base instead of the salt or dye.

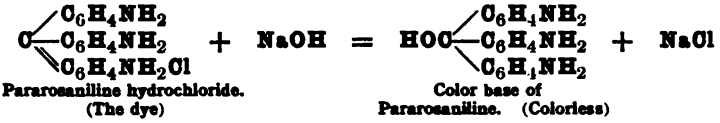
What has been said of the relations of the pararosaniline hydrochloride in its relation to the color base and the leuco base may be applied to rosaniline itself and to the whole class of triphenylmethane dyes.

Leuco Base, Color Base, Pararosaniline

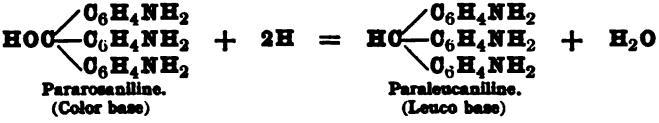
The two terms leuco base and color base are both applicable to derivatives, not only of pararosaniline, but to rosaniline and to a large number of compounds manufactured from both of them. A consideration of the meaning of the terms as applied to pararosaniline will make their meaning clear when applied to any other one of this class of dyes. Neither the leuco base or the color base of pararosaniline has any color at all, and the only difference in composition is that the leuco base contains no oxygen while the color base contains one atom of oxygen. Furthermore, both bases form salts with acids but with this difference, that the salts of the leuco base are colorless while the salts of the color base are colored and form the real dyes. The genetic relation of the three substances will be apparent from the following reactions.

When an alkali is added to a solution of pararosaniline the

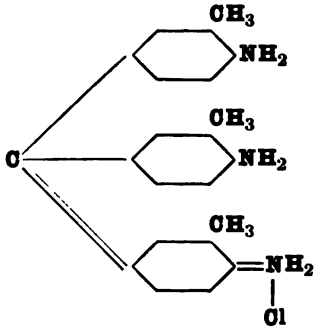
intense color fades away and the color base, the true pararosaniline, is precipitated as follows:


C(C6H4NH2)(C6H4NH2)(C6H4NH2Cl) + NaOH = HOC(C6H4NH2)(C6H4NH2)(C6H4NH2) + NaCl
Pararosaniline hydrochloride. (The dye)
Color base of Pararosaniline. (Colorless)

By reduction of this color base with ammonium sulphide or zinc dust and hydrochloric acid the paraleucaniline or leuco base is produced as follows:



New Fuchsine (1889). Isorubin. In new fuchsine or new rosaniline we have an excellent example of isomerism with Hoffman's violet or at least with one constituent of that dye. New fuchsine is pararosaniline enriched by three methyl groups, and it retains its red color; Hoffman's violet is pararosaniline enriched with three methyl groups, and it is violet. The difference lies in the position of the three methyl groups in the two dyes. In Hoffman's violet they are distributed one in each of the three amino groups of that molecule; in new fuchsine the methyl groups are distributed one to each of the three benzene rings proper, as shown in the following formula:



New fuchsine

New fuchsine is made from orthotoluidine by the new fuchsine process. This process employs formaldehyde to furnish the methane carbon atom of the product instead of depending upon a methyl group of paratoluidine as in the usual method. Formaldehyde is condensed with orthotoluidine to form anhydroformaldehyde-o-toluidine.

$$\underset{\text{Formaldehyde}}{CH_2O} + H_2 \underset{\text{Toluidine}}{NC_6H_4CH_3} = \underset{\text{Anhydroformaldehyde-o-toluidine}}{CH_2NC_6H_4CH_3} + H_2O$$

By heating this product with *o*-toluidine and *o*-toluidine hydrochloride, a rearrangement of the molecule takes place and diaminoditolylmethane results.

$$CH_2{=}\ NC_6H_4CH_3 + \underset{\text{o-Toluidine}}{C_6H_4(CH_3)NH_2} = \underset{\text{Diaminoditolylmethane}}{CH_2[C_6H_3(CH_3)NH_2]_2}$$

When this latter substance is heated with *o*-toluidine hydrochloride and an oxidizing agent new fuchsine is formed, the formula of which is given above.

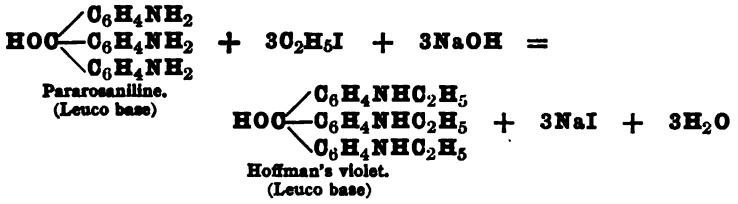
New fuchsine has the advantage of being more soluble than ordinary fuchsine or rosaniline.

Hydrochloric acid in excess turns the solution of new fuchsine yellow, but on diluting with much water the original color returns. A bright red crystalline precipitate is deposited on boiling with sodium hydroxide. The solution in strong sulphuric acid is yellow, which the addition of water changes to red.

Wool, silk, and leather are dyed a rosaniline red, which is brighter and of a bluer tinge than the usual rosaniline shade. Cotton mordanted with tannin and tartar emetic (potassium antimonyl tartrate) is likewise dyed the same shade.

Hoffman's Violet (1863), Red Violet 5R. extra, Violet 4R.N., Violet 5R., Violet R., Violet R.R., Dahlia, Primula R. Under these names, a variety of shades of violet have in the past appeared upon the market. Some are of reddish, others of a bluish violet hue. What the shade will be depends upon the process of manufacture. Any particular shade will be a mixture of methyl or ethyl compounds of pararosaniline and rosaniline.

The red color of these two latter substances becomes a violet by implanting in them methyl or ethyl groups in place of the amino hydrogen atoms. Selecting pararosaniline and ethyl iodide as representing the process, the reaction may proceed as follows:



In the manufacture, an alcoholic solution of pararosaniline and rosaniline is treated with caustic soda and ethyl iodide. The greatest number of methyl or ethyl groups which can be fixed in this way is three: one in each amino group. The more completely the methylation is carried on up to this limit the bluer the shade becomes. Less complete methylation gives redder shades of violet. Monomethyl or dimethylrosaniline would be therefore redder than the trimethyl derivative. A bluer shade may also be produced by introducing ethyl groups in place of methyl groups. This accounts for some of the different marks used in the trade.

The hydrochloride is the salt used in dyeing. It has had a serious rival in methyl violet B. which has almost driven it from the market.

Methyl Violet B. and 2B. (1861), Paris Violet. Violet 3B., Malberry Blue. This is a mixture of two substances, one a pentamethyl pararosaniline, the other a hexamethyl pararosaniline. The purest dimethylaniline, $C_6H_5N(CH_3)_2$ when oxidized by cupric chloride produces methyl violet B.

In the actual manufacture, there are mixed together dimethylaniline, cupric chloride, acetic acid, potassium chlorate and a large amount of common salt. Later processes omit the potassium chlorate and employ phenol in place of the acetic acid. In any case, the cupric chloride is reduced to cuprous chloride; this is then changed back to cupric chloride. It thus acts as an oxygen carrier during the process. The

cuprous chloride unites to form an insoluble compound with the dyestuff as it is produced. This was formerly decomposed by hydrogen sulphide and the soluble dye separated from the insoluble copper sulphide. At present ferric chloride decomposes the double salt changing the cuprous to cupric chloride which remains in the mother liquor while the methyl violet B. is precipitated by the dissolved salt.

It is not known what special function the phenol exercises in the process for methyl violet B.; but the yield is for some reason greater than with the acetic acid it replaces.

Dimethylaniline would not seem to furnish any methane carbon as a necessary nucleus; but it in fact yields one of its methyl groups for this purpose.

The reaction may proceed as follows:

$$3C_6H_5N(CH_3)_2 + 3O + HCl = C\begin{cases} C_6H_4NHCH_3 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2Cl \end{cases} + 3H_2O$$

Dimethylaniline — Methyl violet B.

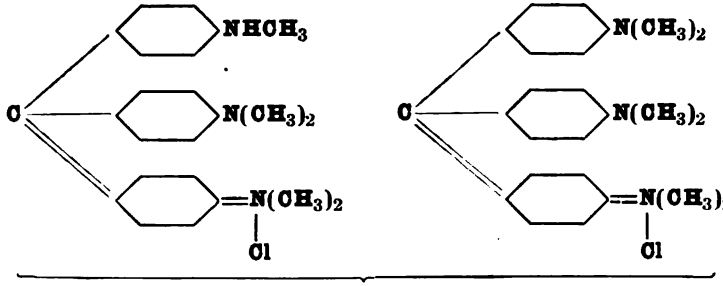
It is of interest to note that oxidation of dimethylaniline will not take place in acid solution with lead peroxide, manganese dioxide or chromic acid. In direct contrast to this, is the successful oxidation of dimethylaniline in conjunction with tetramethyldiaminodiphenylmethane to form the same dye methyl violet B.

Methyl violet B. is a shining metallic green powder which easily dissolves in water or alcohol to a violet solution. Silk and wool are dyed directly and cotton after mordanting with tannin and tartar emetic. It is frequently used with other colors to improve and beautify the shade.

Hydrochloric acid produces first a blue color, then a green and by adding more acid a deep yellowish brown. Sodium hydroxide causes a brownish red color and a precipitation of the color base, of the same color. It dissolves in strong sulphuric acid with a yellow color which the gradual addition of water turns yellowish green, then greenish blue and at last violet.

The actual dye contains also hexamethylpararosaniline, and the more this latter component is present, that is the

greater the number of methyl groups present, the bluer the shade of violet. The two components are represented below:



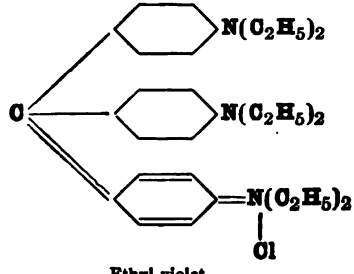
Methyl violet B and 2B.

Ethyl Violet. This dye is a derivative of pararosaniline. Within the formula of pararosaniline there are six hydrogen atoms in three amino groups; these are all replaceable by other radicals or groups of atoms and in this particular case all six hydrogens have been replaced by six ethyl groups. The color of the dye changes under the influence of the ethyl groups from magenta to violet.

In its manufacture, pararosaniline is not first made and then the ethyl groups, as in the preparation of Hoffman's violet, but diethylaniline, already carrying two ethyl groups in its amino groups employed. Three molecules react with one molecule of phosgene, $COCL_2$, as follows:

$$3C_6H_5N(C_2H_5)_2 + COCl_2 = C[C_6H_4N(C_2H_5)_2]_3Cl + HCl + H_2O$$

The constitutional formula shows the pararosaniline nucleus contained within it.



Ethyl violet.
Hexaethylpararosaniline hydrochloride

Ethyl violet is a green crystalline powder which dissolves easily in water to a violet blue color. Wool, silk, and cotton which has been mordanted with tannin are dyed from a luke-warm bath.

Hydrochloric acid turns the aqueous solution reddish yellow. Sodium hydroxide produces a grayish violet precipitate which on heating melts together to form a brown oil; the solution becoming in the meantime colorless.

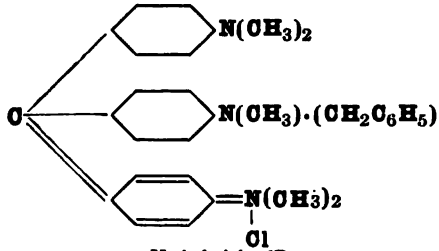
The dye dissolves in strong sulphuric acid to form a brownish yellow solution, which is changed to green by the addition of a liberal amount of water.

Methyl Violet 6B. (1868), Paris Violet 6B., Benzyl Violet. This is the bluest shade of the methyl violets and the mark 6B. stands for a dye in which the blue shade is the deepest of the commercial brands. Methyl violet itself is a mixture of penta- and hexamethylrosaniline. Now it has been found that benzyl chloride, $C_6H_5CH_2Cl$, will react with methyl violet, producing a substance enriched by a benzyl group ($C_6H_5CH_2$).

Formerly it was supposed that the benzyl group was capable of driving out the methyl groups already established in the molecule. O. Fischer has proved that no methyl group is disturbed, and that it is hydrogen alone which has remained unreplaced in an amino group which can be exchanged for a benzyl group.

Thus it will at once be understood why it is that hexamethylpararosaniline, a constituent of methyl violet, containing no hydrogen in its amino groups, cannot react with benzyl chloride and so enrich itself with a benzyl group. Pentamethylrosaniline can react by exchanging its single amino hydrogen for a benzyl group, which develops a bluer shade in the dye.

The constitutional formula is shown below:



Methyl violet 6B.

The marks 2B., 3B., 4B., and 5B. are simply mixtures in varying proportions of the marks B. and 6B.

The dyestuff has a brownish shade and a metallic bronzy lustre. It comes either in lumps or powder. The hydrochloride, and the hydrochloride as a double salt with zinc chloride are the commercial forms.

Fibres dyed with methyl violet become reddish violet when treated with sodium hydroxide: methyl violet 6B., with sodium hydroxide, turns light blue: on standing, both solutions lose their color.

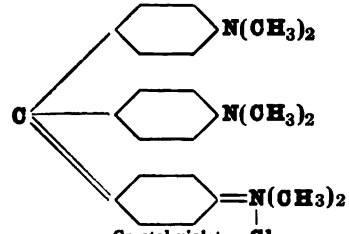
Crystal Violet (1883), Crystal Violet O., Crystal Violet, Violet C., Violet 7B. Extra. This dye was given its name on account of the size and beauty of its crystals. It is a hexamethyl derivative of pararosaniline. The effect of implanting six methyl groups in the red dye is to change it to violet. The methylation of pararosaniline by acting upon it with methyl iodide cannot be carried further than to form a trimethyl compound, as was stated under Hoffman's violet.

Another process is employed. One among others for attaining the same object employs dimethylaniline, $C_6H_5N(CH_3)_2$, and phosgene, $COCl_2$. Each molecule of dimethylaniline contains two of the requisite six methyl groups and by the action of phosgene (to supply the methane carbon) on three molecules of dimethylaniline the color base is developed in accordance with the following reaction:

$$COCl_2 + 3C_6H_5N(CH_3)_2 = HOC(C_6H_4N(CH_3)_2)_3 + 2HCl$$

Phosgene — Dimethylaniline — Color base: Crystal violet

The color base reacting with the hydrochloric acid produces the dye, the formula of which is given below:



Crystal violet.
Hydrochloride of hexamethylpararosaniline

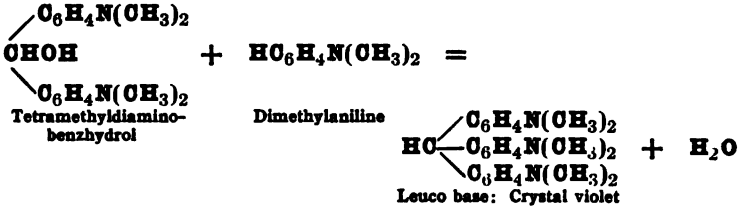
As the influence of methyl groups entering the red molecule of pararosaniline is to produce first a violet and then a bluer shade in proportion to the number of methyl groups, this dye, containing the maximum number that can possibly enter the molecule, gives in dyeing a pure and very blue shade of violet.

The dyestuff appears as bronze glistening crystals, which easily dissolve in water and alcohol to a violet blue color.

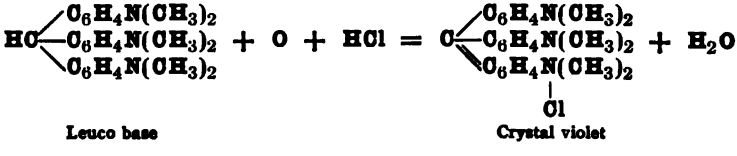
Hydrochloric acid causes first a change of shade to blue, then green and finally yellow. A violet precipitate falls on adding caustic soda. Strong sulphuric acid forms a yellow solution of the dye which the addition of water gradually converts to green, blue, and lastly to violet.

Silk and wool, and tannin-mordanted cotton are dyed a bluish violet.

Another method of formation consists in the condensation of one molecule of tetramethyldiaminobenzhydrol with one molecule of dimethylaniline. The leuco base thus produced is oxidized and the hydrochloric acid salt formed to develop the dye. Here, as before, the six methyl groups needed are provided in the factors of the reaction as represented below:



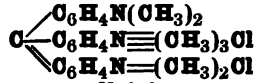
Oxidation in acid solution would develop the color base and the salt would be formed, at once developing the bluish violet of the dye.



Methyl Green (1871), Paris Green, Light Green, Double Green. Methyl violet is the basis of methyl green; for,

on treating the former, which is a hexamethylpararosaniline, with methyl chloride, an addition of a methyl group and a chlorine atom takes place, forming a heptamethylpararosaniline. A change from violet to green accompanies the change from the hexamethyl to the heptamethyl compound.

In the manufacture, it is only necessary to pass the vapor of methyl chloride through a solution of methyl violet in alcohol kept at a temperature of 40°, and the methyl chloride decomposing attaches both its methyl group and chlorine to a dimethylamino group of the dyestuff. The alcohol is carefully distilled off, water added to dissolve the product and by addition of chalk and salt the methyl green is precipitated, having a composition shown by the formula:



Methyl green. Heptamethylpararosaniline chloride

The zinc chloride double salt is the most common commercial form; it appears in green crystals.

The dyestuff dissolves easily in water; a spot on paper will turn violet on drying and heating, strongly indicating a separation of methyl chloride and a regeneration of methyl violet from which it was formed. The dyestuff heated to 110–120° gradually loses methyl chloride and becomes violet. This property leads to its detection on a fabric, for if a portion of the green material on heating to 120° turns violet methyl green was the original of the dyestuff.

The more intense coloring power and cheapness has caused malachite green to almost completely replace methyl green in the dyehouses.

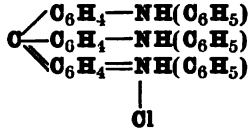
Methyl Violet, as an impurity of methyl green, may be detected by shaking the dyestuff with amyl alcohol, wherein the methyl violet is soluble and communicates its own violet color to the solution; the methyl green remains insoluble. Here is an instance where silk may be dyed green directly but wool must be mordanted by immersing in a bath of sodium hyposulphite rendered acid, so that the finely divided

sulphur may impregnate the fibre, forming a mordant; then the wool will take the green color. Tannin-mordanted cotton is dyed green.

Picric acid, $C_6H_2(NO_2)_3OH$, forms a soluble precipitate in aqueous solution; it dissolves in alcohol, however, and is known as "spirit-soluble green."

Ethyl Green (1866). If methyl violet is treated with ethyl bromide, an ethylhexamethylrosaniline is formed similar in its properties and reactions to methyl green, and, as a matter of fact, it was discovered five years before methyl green.

Aniline Blue (1860), Opal Blue, Gentian Blue 6B., Fine Blue, Hessian Blue. When pararosaniline (and rosaniline) are treated with an excess of aniline in the presence of benzoic acid, the hydrogen atoms of the amino groups are successively replaced, forming mono-, di-, and triphenyl derivatives of of pararosaniline, which result according to the length of time consumed in the process. Purest aniline blue, characterized as opal blue, is a triphenylpararosaniline, one phenyl group distributed to each amino group as shown in the following formula:



Aniline blue (spirit soluble).
Hydrochloride of triphenylpararosaniline

Three phenyl groups are all that can be introduced into the pararosaniline (or rosaniline) molecule by the process of manufacture described below.

When only one or two phenyl groups enter the larger molecule the shade inclines to violet.

During the manufacture, the amino group of the aniline, which is to furnish the entering phenyl group, escapes as ammonia. The function of the benzoic acid is obscure. Rosaniline, without the acid being present, does not react with aniline and yet a very small amount is sufficient to facilitate the process. At the end of the reaction the benzoic

remains unchanged and can be recovered by the use of an alkaline solution with but slight loss.

Yet the employment of a larger amount of acid does not hasten the phenylation of the rosaniline, but a larger excess of aniline (ten times the theoretical amount) does hasten the action and thus save time. It also has the effect of making the product entirely a triphenyl rosaniline free from the monophenyl and diphenyl compounds.

If higher homologues of aniline are present, a reddish shade of blue results. So necessary is pure aniline for the attainment of the purest blue, that a specially prepared grade is made available in commerce known as aniline for blue.

When ordinary rosaniline which contains both pararosaniline and rosaniline is used, it is found that the former acquires the phenyl groups more quickly than its higher homologue: if the operation is pushed to the end until the rosaniline molecule is itself completely phenylated, then some of triphenylpararosaniline first formed is found to have meanwhile partly decomposed. A pure blue is not easily obtained from the mixture.

The commercial process is carried out in an iron kettle provided with a stirrer and a distillation outfit. A mixture of rosaniline base, benzoic acid, and aniline is charged into the kettle and the mass heated to the temperature of boiling aniline. Since the product of this reaction is colored, its progress can be determined by the development of the color. A test portion is withdrawn and dissolved in alcohol acidified with acetic acid. When this develops the proper shade, the process is interrupted. Too long heating causes a partial decomposition of the product. From two to four hours' heating usually suffices. The melt is partially neutralized with hydrochloric acid, which causes the separation of the hydrochloride of triphenylrosaniline almost chemically pure, while the solution of aniline in aniline chloride keeps the impurities in solution.

This process has completely superseded the one producing a more impure product and removing the impurities with alcohol. The lower phenyl derivatives of rosaniline are

soluble in alcohol while the triphenyl compound is insoluble.

The hydrochloride salt forms a bronzy powder: the sulphate or acetate is a bluish powder. The dyestuff is insoluble in water, but the acetate easily soluble in alcohol, the sulphate and hydrochloride with more difficulty.

Hydrochloric acid causes no change to the alcoholic solution of the dye. A brownish red shade follows the addition of caustic soda to the same solution. It dissolves in strong sulphuric acid with a brownish yellow color: the dilution of this with water produces a blue precipitate.

Aniline blue has been employed for dyeing wool, silk, and cotton: also for coloring paper pulp and lacquers. It is principally used for conversion into a soluble sulpho acid derivative by treating with sulphuric acid.

Diphenylamine Blue (1866) (spirit soluble), **Bavarian Blue** (spirit soluble), **Direct Blue.** Oxalic acid acting upon diphenylamine, $(C_6H_5)_2NH$, produces triphenylpararosaniline. It differs from aniline blue being a pure triderivative of pararosaniline, while aniline blue is a mixture of triphenyl derivatives of both pararosaniline and rosaniline (while mono- and di-derivatives may also be present).

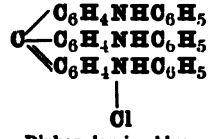
The following equation exhibits the reaction:

$$\underset{\text{Diphenylamine}}{3(C_6H_5)_2NH} + C_2H_2O_4 = CO_2 + 2H_2O + \underset{\text{Diphenylamine blue}}{CH(C_6H_4)_3N_3H_3(C_6H_5)_3}$$

Washing the product removes any unchanged oxalic acid and boiling with alcohol removes any diphenylamine remaining.

The residue is converted to the hydrochloride salt and purified.

Diphenylamine blue is of a finer quality than aniline blue, but more exepnsive. Its constitution appears below:



Diphenylamine blue.
Hydrochloride of triphenylrosaniline

Its cost is increased from the fact that only about 10 per cent of the diphenylamine is actually converted into coloring matter by the process.

The dyestuff appears as a brown powder. It is insoluble in water, sparingly soluble in cold alcohol, but easily in hot. The reactions with acid and alkali are similar to those for aniline blue, and like that dye it is chiefly converted into a soluble blue dye by conversion into a sulpho acid with sulphuric acid.

Night Blue (1883), is related to the two preceding dyes, in so far as its nucleus is diphenylnaphthylmethane. It is produced when tetraethyldiaminobenzophenone chloride acts upon paratolyl-α-naphthylamine as follows:

$$\begin{matrix} C_6H_4N(C_2H_5)_2 \\ CCl_2 \\ C_6H_4N(C_2H_5)_2 \end{matrix} + C_{10}H_6NHC_6H_4CH_3 =$$

Tetraethyldiamino-benzophenone chloride — Paratolyl-α-naphthylamine

$$\begin{matrix} C_6H_4N(C_2H_5)_2 \\ C{-}C_6H_4N(C_2H_5)_2 \\ C_{10}H_6NH(C_6H_4CH_3)\cdot HCl \end{matrix} + HCl$$

Night blue

A peculiar property of this dye is its facility of forming insoluble compounds with other dyes, e.g., picric acid, naphthol yellow S., and many others. It may on this account be used to estimate these dyes quantitatively.

Night blue owes its name to its especial beauty under artificial illumination. It occurs in commerce as a violet powder with a bronze lustre. In water it dissolves easily with a violet blue color. Wool and silk are dyed a very pure shade of blue which is fast to soap, but unfortunately fugitive to light. Hydrochloric acid forms a precipitate in aqueous solution, but further addition of the acid causes it to dissolve to a yellowish brown solution.

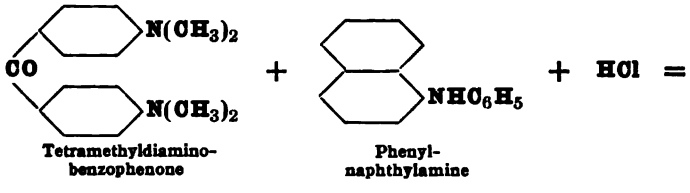
Caustic soda causes the color base to fall as a pale reddish brown precipitate. It forms a yellowish brown solution in concentrated sulphuric acid which changes first to green and then to blue by adding water.

Victoria Blue B. (1883). In this dyestuff one of the phenyl groups which is present in the pararosaniline nucleus is replaced by naphthyl, the radical of naphthalene, as phenyl is the radical of benzene. The nucleus of this dyestuff is then diphenylnaphthylmethane. There are several dyes which bear a similar relation to diphenylnaphthylmethane.

Victoria Blue B. is an example of such a dye. It is often classed as a phosgene dye, because the methane carbon is furnished by phosgene, $COCl_2$. Phosgene and dimethylaniline react in the presence of $AlCl_3$, according to the following equation, to form tetramethyldiaminobenzophenone:

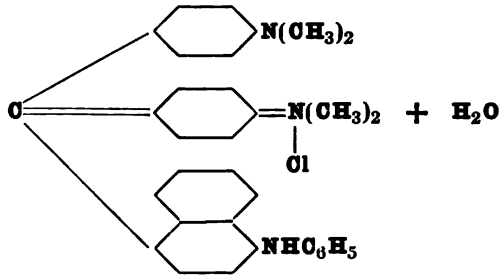
$$\underset{\text{Phosgene}}{COCl_2} + 2\underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} = \underset{\substack{\text{Tetramethyl-}\\\text{diaminobenzo-}\\\text{phenone}}}{CO[C_6H_4N(CH_3)_2]_2} + 2HCl$$

By melting tetramethyldiaminobenzophenone with phenyl-α-naphthylamine and phosphorus oxychloride, the Victoria blue B. is formed as shown below:



Tetramethyldiamino-benzophenone

Phenyl-naphthylamine



Victoria blue B.

In commerce, this dye appears as a violet powder or shining grains, which are sparingly soluble in cold water but more easily in hot. If its deep blue aqueous solution is boiled, the liquid becomes turbid, owing to the separation of the

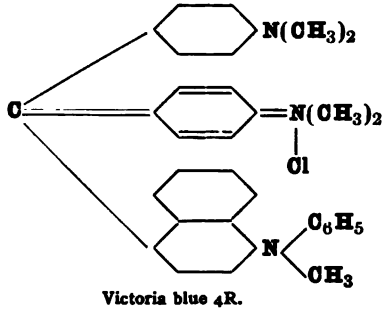
free color base which settles out as a reddish brown precipitate. Acetic acid will prevent this decomposition.

The addition of sulphuric acid to its aqueous solution turns it from blue to green and then to orange; but the original blue returns on neutralizing the acid. This change is supposed to be due to the formation of salts having more than one equivalent of acid. Hydrochloric acid first causes a blue precipitate, then it changes to green and finally to a dark yellowish brown. A dark reddish brown precipitate falls on adding caustic soda.

Wool and silk are dyed from a bath containing acetic acid. Cotton may also be dyed directly from an acetic acid bath; or it may be dyed after first mordanting with tannin and tartar emetic. The blue imparted to fabrics is moderately fast to soap and milling, but shows less resistance to light.

Reducing agents transform this dye into its leuco base, which will again yield the blue dyestuff by oxidation in acid solution. The blue color on the fabric changed to reddish brown by sulphuric acid is restored by washing in water.

Victoria Blue 4R. This dyestuff is in many respects similar to the preceding. It is formed from the same compound, tetramethyldiaminobenzophenone; or from tetramethyldiaminobenzhydrol, which differs from it by an accession of two hydrogens. Combination takes place between this and methylphenyl-α-naphthylamine in a reaction very similar to that for Victoria blue B. The graphical formula shows its difference from that dye.



Victoria blue 4R.

The presence of a methyl group in this blue dye in place of a hydrogen of Victoria blue B. has the effect of producing a redder shade of blue. In its properties and application it resembles Victoria blue B. Victoria blue 4R. appears either as a powder of a bronze lustre, or, if from a melted condition, of a yellowish bronze reflex. Caustic soda causes a brownish violet precipitate to separate.

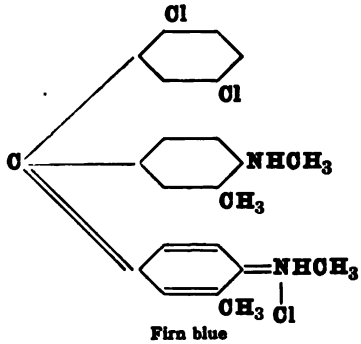
Firn Blue (1892), **Glacier Blue.** This blue dye has the same empirical composition as Victoria green 3B., and is a good illustration of isomeric substances of different color, one green, the other blue. Victoria green 3B. contains four methyl groups distributed into two amino groups. Only two of the four methyl groups in firn blue are in the amino groups; the other two are joined directly to benzene rings. Thus instead of dimethylaniline, $C_6H_5N(CH_3)_2$, monomethylorthotoluidine, $C_6H_4(CH_3)NHCH_3$, is allowed to act upon dichlorbenzaldehyde, $C_6H_3Cl_2CHO$, as follows:

$$\underset{\text{Dichlorbenzaldehyde}}{C_6H_3Cl_2CHO} + \underset{\text{Monomethylorthotoluidine}}{2C_6H_4CH_3NHCH_3} =$$

$$HC\begin{cases} C_6H_3Cl_2 \\ C_6H_3CH_3NHCH_3 \\ C_6H_3CH_3NHCH_3 \end{cases} + H_2O$$

Leucofirn blue

Oxidation of this leuco base and formation of its chloride develops the dye from this.



Firn blue

The zinc chloride double salt appears in commerce as a reddish violet powder of a lustre like copper. Its solution in

water is greenish blue, and on cooling it gelatinizes. It dyes silk and wool a greenish blue; cotton is mordanted with tannin before dyeing.

It is a beautiful color which is fast to washing and light.

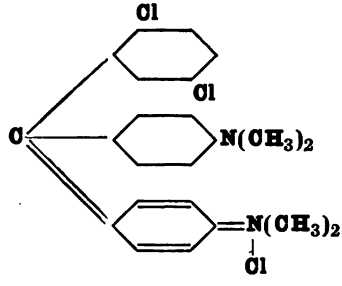
Hydrochloric acid produces a dark green precipitate which changes to yellow with further addition of the acid. A yellowish orange turbidity follows the addition of caustic soda. Strong sulphuric acid dissolves the dye to a yellow solution, from which the addition of water separates out a green precipitate.

Victoria Green 3B. (1883), New Fast Green 3B., New Solid Green B.B. and 3B. has the same composition as malachite green, with the exception of two atoms of chlorine. The effect of these two chlorine atoms is to give a bluer shade of green. The chlorine atoms are already fixed in the dichlorbenzaldehyde, which acts upon dimethylaniline as follows:

$$C_6H_3Cl_2CHO + 2C_6H_5N(CH_3)_2 = HC(C_6H_3Cl_2)(C_6H_4N(CH_3)_2)(C_6H_4N(CH_3)_2) + H_2O$$

Dichlorbenzaldehyde — Dimethylaniline — Leuco Victoria green

By oxidation and formation of the chloride, the dye is developed; its constitution is shown below:



Victoria green 3B.
Hydrochloride of tetramethyl-diaminodichlortriphenylmethane

The double salt of this with zinc chloride is the commercial dye which appears as a green glistening crystalline powder. It is sparingly soluble in cold water but more easily in hot. Alcohol dissolves it readily. The hot aqueous solution gelatinizes on cooling.

Hydrochloric acid turns it yellowish green, then yellow. The solution is turned a reddish yellow, and a slight precipitate falls on the addition of caustic soda.

Wool, silk, and tannin-mordanted cotton are dyed a bluer shade of green than with malachite green.

Malachite Green (1877), **Benzaldehyde Green, New Victoria Green, New Green, Fast Green, Vert Diamant, Bitter Almond Oil Green, Benzoyl Green, Benzal Green, Diamond Green, and Dragon Green** are all names of a beautiful green dye which at one time was manufactured in large quantities.

The first of these two names suggests its resemblance to the magnificent green Russian mineral malachite, and the second recalls the substance used in one method of preparation. The chemical name which reveals its structure is tetramethyldiaminotriphenylmethane hydrochloride. A careful inspection, later, of the graphical formula of this substance will show the significance of each syllable of this name.

One process, and the one which gave this dye the name of benzaldedyde green, consists in heating together one molecular equivalent of benzaldehyde, C_6H_5CHO, and two equivalents of dimethylaniline, $C_6H_5N(CH_3)_2$, with anhydrous zinc chloride. As these formulas are examined, they will be found to be benzene rings which are already possessed of the side groups that really appear in the larger complex molecule of the dye.

Benzaldehyde furnishes in its side group the carbon

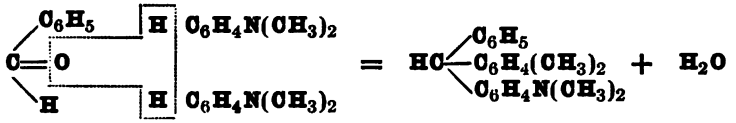
atom which is to become the methane carbon uniting the three benzene rings of the dye molecule. The dimethylaniline exhibits benzene rings enriched not only with the requisite amino groups, but these groups are possessed of the requisite methyl groups.

The oxygen of the benzaldehyde unites with a single hydrogen from each of the two molecules of dimethylaniline, forming water which is then attracted and held by the anhydrous zinc chloride. The zinc chloride thus stimulates the reaction by its attraction for water.

The residues of the larger molecules unite, being held by the single carbon atom brought into the reaction in the side group of the benzaldehyde. The reaction is as follows:

$$C_6H_5CHO + 2C_6H_5N(CH_3)_2 = CH[C_6H_4N(CH_3)_2]_2C_6H_5 + H_2O,$$

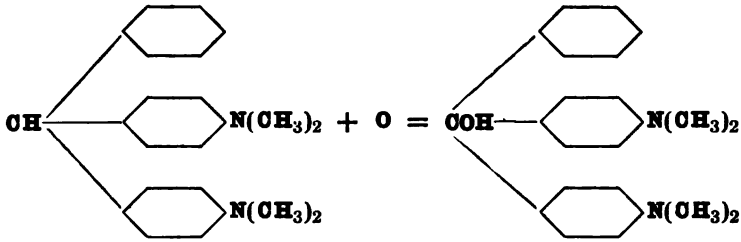
or graphically,



Benzaldehyde Dimethylaniline Leuco malachite green

In the process of manufacture the two substances, both of which are liquid, are heated together with zinc chloride, sulphuric acid, or anhydrous oxalic acid, which facilitates the reaction by causing the separation of water. The mixture is constantly stirred and becomes thick and pasty. The product, which is the leuco base, is dissolved in hydrochloric or acetic acid and oxidized by the addition of lead peroxide.

This oxidation thrusts a single oxygen atom between the carbon and hydrogen atoms of the methane nucleus and thus changes the leuco base into the color base as follows:

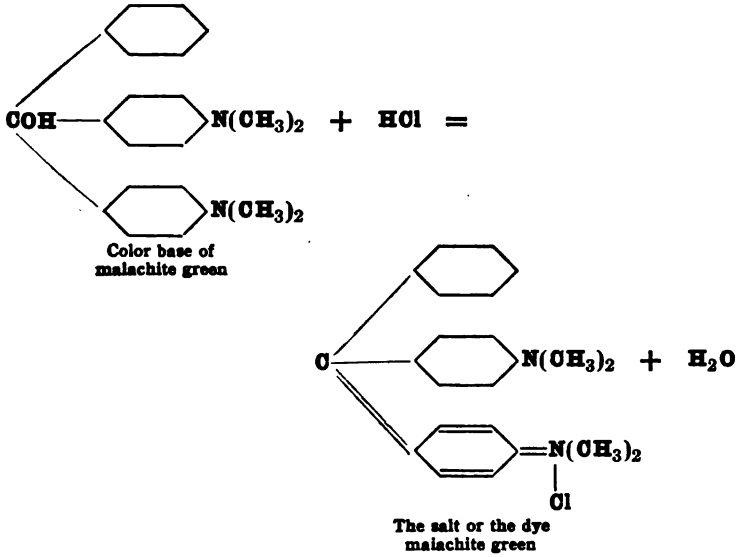


Leuco base of malachite green

Color base of malachite green

The lead is afterwards precipitated and removed as sulphate by the addition of sodium sulphate. The hydrochloric acid present in the solution acts at once upon the color base, forming water and converting it into the hydrochloride—a salt which is the dye itself. The chlorine does not attach itself to the carbon from which the OH group was removed to

form water; but by a rearrangement of valences, it becomes joined to a nitrogen atom. This arrangement, known as the quinone structure (because it occurs in the substance quinone), is shown below:



From the solution in which the dye was formed it is precipitated by zinc chloride and common salt, whereby the double salt of the dye and zinc chloride is formed. This, being insoluble in a salt solution, falls as a precipitate. It is filtered off, recrystallized from hot water, and is then ready for the market.

The double salt is the form met with in commerce as brass yellow crystals of the following composition $(C_{23}H_{25}N_2Cl)_3$, $2ZnCl_2 2HO$.

The oxalate, $(C_{23}H_{25}N_2Cl)_2 3C_2H_2O_4$, in metallic green glistening plates, is also a commercial form of the dye.

Other methods beside that given above have been used on a commercial scale, and the varying cost of raw materials often render alternative processes necessary; as the following account will show. Malachite green was first obtained by Otto Fischer from tetramethyldiaminotriphenylmethane by

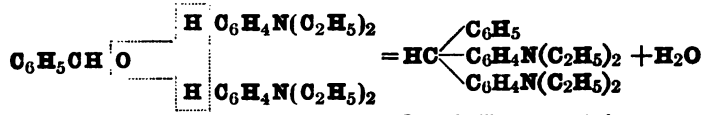
oxidation. A short time afterward, Doebner obtained it by the action of benzotrichloride, $C_6H_5CCl_3$, on dimethylaniline. This process was patented and used on a commercial scale. The manufacture by Fischer's method did not seem possible on account of the cost of benzaldehyde, C_6H_5CHO, which he needed as a starting-point. The difficulties in making benzaldehyde were later overcome, however, and so much cheaper was it finally produced that now Fischer's process is used commercially, and the benzotrichloride, which never gave very good results, is entirely abandoned.

Silk is dyed from a pure soap bath and brightened with acetic acid. Wool is dyed in a weak acid bath. Cotton first requires mordanting with tannin and tartar emetic.

Concentrated hydrochloric acid gives an orange color which changes back to the original green when treated with much water. Acetic acid removes the color with a bluish green tint. Ammonia and alkalies decolorize it completely. Heat does not change this color, while methyl green becomes violet.

Brilliant Green (1879), Malachite Green G., New Victoria Green, Ethyl Green, Emerald Green, Fast Green J., Diamond Green J., Solid Green J., Solid Green J.J.O., Brilliant Green, is a close relative of malachite green, for an examination of its structure reveals ethyl groups in place of the four methyl groups of the latter. This change in composition has the effect of producing a yellower shade of green than malachite green.

It is manufactured from benzaldehyde and diethylaniline in accordance with the equation:

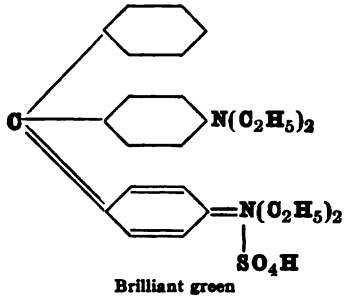


A change in color from green to reddish yellow takes place when hydrochloric acid is added in sufficient amount to the

concentrated aqueous solution. Sodium hydroxide decolorizes the solution and causes the color base to separate out as a pale green precipitate.

It dissolves in strong sulphuric acid to a yellow solution, which on gradually diluting with water passes from yellow to a reddish yellow, yellowish green, and finally green.

Oxidation and formation of the sulphate produces the dyestuff as given below:

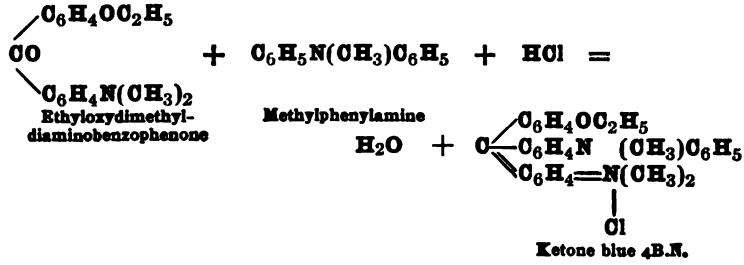


Brilliant green

This is employed for dyeing silk, wool, jute, leather, and cotton mordanted with tannin and tartar emetic. The shade is yellower than that of malachite green.

Ketone Blue 4B.N. (1890), is a dyestuff containing oxygen, those so far described in this class having had no oxygen in their composition. It is a triphenylmethane derivative and possesses an ethylated hydroxyl group in one of its three benzene rings.

It is made by bringing together ethyloxydimethylaminobenzophenone and methylphenylamine with some hygroscopic substance to remove the water formed.



Ketone blue 4B.N. belongs to a new and important class of dyes termed Patent Blues, to be discussed later, which are fast to alkalies, and this valuable property was ascribed to the presence of the hydroxyl group, represented here by the ethyl-oxy group. Further investigation did not confirm this view, however, and their fastness to alkalies depends upon another feature of their composition.

The dyestuff appears in reddish violet grains. Both in water and alcohol it dissolves easily to a violet color. It is used for dyeing silk and wool. Hydrochloric acid decolorizes the solution of the dye, while sodium hydroxide turns the liquid brownish red. The solution in strong sulphuric acid is yellow and changes to green on dilution with water.

Sulphonic Acids of the Triphenylmethane Dyes

The discovery made by Nicholson in 1862 that insoluble aniline blue on treatment with fuming sulphuric acid still retained its color and became soluble was of far greater importance than making this particular dyestuff available in soluble form. The method was found applicable to a large number of dyes, making them available through increase in their solubility and converting basic dyes into acid dyes, which further increased their range and usefulness.

By treatment with sulphuric acid the group $-SO_3H$, called the sulphonic acid group, becomes substituted in the molecule of the dyestuff and converts it into a sulphonic acid derivative.

The tinctorial power of the dye is not increased by this treatment; indeed, it is sometimes diminished one-half, but the dye has become an acid dyestuff, and its value, especially for wool dyeing, much enhanced.

The sulphonic, or sulpho group, as it may be used in shortened form, may be introduced into the molecule, either by treating with sulphuric acid the finished dyestuffs, or their leuco bases before oxidation; or the components

may be sulphonated previous to their combination into a dye.

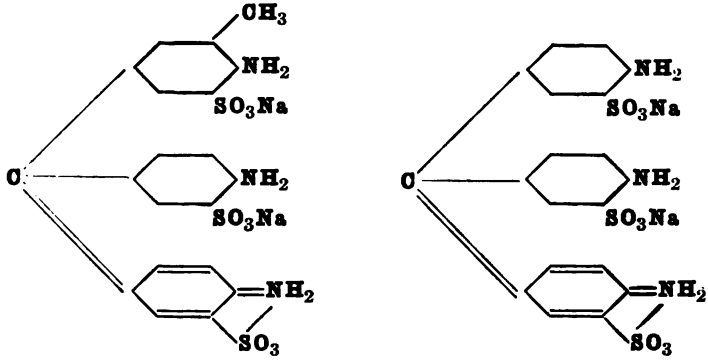
A difference in the case of sulphonation of some dyes allows direct conclusions to be drawn in regard to their structure, e.g., rosaniline can be sulphonated with difficulty, but aniline blue, which is a triphenyl rosaniline, is sulphonated so easily that only gentle warming with moderately concentrated sulphuric acid is sufficient to introduce the sulpho group.

(The following formulas show which benzene rings are most easily sulphonated.) The ease of sulphonation of the aniline blue shows that the sulpho groups enter the outer three phenyl groups which have replaced the amine hydrogen atoms.

Acid Magenta (1877), Fuchsine S., Acid Fuchsine, Acid Roseine, Acid Rubine, Rubine. Acid Magenta is a sulphonic acid derivative of magenta and magenta is a mixture of rosaniline and pararosaniline. Commercial magenta or rosaniline was discovered in 1856. The amino groups gave a basic character of the dye, and it was applied in the usual manner for basic dyes. Twenty-one years later the treatment of this basic dye with concentrated sulphuric acid caused the fixation of three sulphonic acid groups in the molecule. From their strongly acidifying power the product became an acid dyestuff. The color imparted by this acid dye is not different from that given by the basic magenta, but it has only about half as great tinctorial power. Some corresponding advantage must offset this loss of coloring power, and it consists in this, that it is more soluble, and the dye can be employed in strongly acid baths and also combined with other dyes and mordants.

It is used for silk and wool, but not for cotton. Dried commercial magenta treated with fuming sulphuric acid at 100–170° acquires a sulphonic group in each of the phenyl groups and a trisulphonic acid of magenta results; or since this is a mixture of rosaniline and paraosaniline so this compound of magenta is likewise a mixture of the trisulphonic

acids of both rosaniline and pararosaniline. The sodium salt of this dye is shown below:



Sodium salts of rosaniline and pararosaniline trisulphonic acids

This dyestuff has the appearance of a green metallic powder. Water dissolves it easily, but it is almost insoluble in alcohol. The normal salts are colorless; the acid salts are red.

From the color of the acid salts and the lack of color of the normal salts, a conclusion is drawn that a kind of salt-forming union exists between the sulphonic acid group and the basic amino group of one of the benzene rings as shown in the formula above, and furthermore that in the colorless normal salts that a carbinol group is present, or in other words, that the central methane carbon, by the fixation of a hydroxyl group, becomes a carbinol group exactly analogous to that of the white rosaniline color base with its carbinol group.

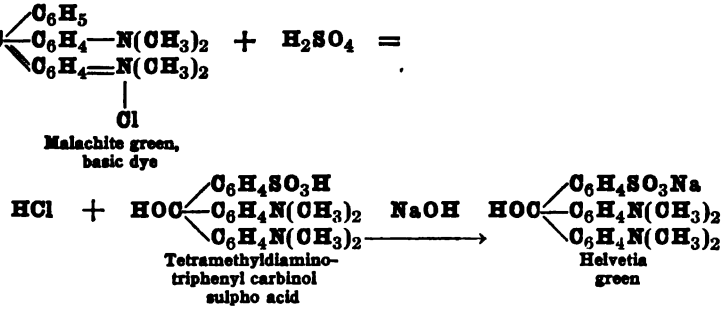
Acid magenta on the fibre may be recognized as different from magenta by applying a mixture of equal parts of water and hydrochloric acid. Acid magenta is not changed, while magenta is decolorized; the little acid magenta which dissolves from the fibre, forming a cherry red color in the solution, need cause no confusion.

No change in the color of its solution is caused by hydrochloric acid. Caustic soda almost completely decolorizes it; but, on later adding acids the original color returns. Even carbonic acid will effect this change. Its yellow solution in strong sulphuric acid is turned gradually red by water.

Acid magenta has been used to color wines, and it is not so easily detected as common magenta because it will not dissolve in ether, nor will it combine with stearic acid, which are used in detecting ordinary magenta.

SULPHONIC ACIDS OF THE DIAMINOTRIPHENYLMETHANE DYES

Helvetia Green (1878), Acid Green. The first acid dye of this group was produced in 1878 and was known under the names of acid green and Helvetia green. It was prepared by treating malachite green with sulphuric acid. One sulphonic acid group was thus introduced into that benzene ring which possesses no amino group.



This dyestuff is no longer used and is noted here as the first sulphonic acid compound of its class and as the simplest example of sulphonation.

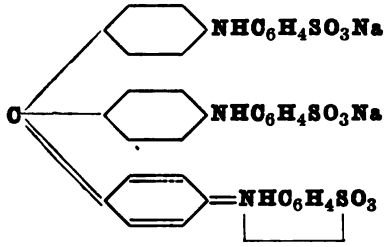
Soluble Blue (1862), Water Blue, Cotton Blue, Navy Blue, London Blue Extra. Aniline blue on being sulphonated at 30–35° forms alkali blue, but if three to four times its weight of sulphuric acid and a temperature of 60°, and a final temperature of 100–110° be employed, then a further sulphonation occurs and a soluble blue is formed.

Three sulphonic acid groups are thus introduced one into each aminophenyl group of the molecule. After cooling, the strongly acid solution is poured into three to four times its volume of water to precipitate the coloring matter. It is filtered off and dissolved in a large amount of boiling water; the excess of sulphuric acid cautiously neutralized by milk

of lime. After filtering off the calcium sulphate, the filtrate to which some carbonate of soda or ammonia has been added is evaporated to dryness.

Soluble blue is a mixture of the sodium, ammonium or calcium salts of the trisulphonic (with a little disulphonic) acids of triphenylpararosaniline and rosaniline. The ammonium salt forms a mass of the lustre of copper; while the sodium salt occurs in dark blue lumps.

The constitution of the dye is apparent from the triphenyl pararosaniline derivative here given:



Soluble blue
(when mixed with the rosaniline derivative)

This dye is of advantage in producing compound colors on silk and wool. It differs from alkali blue in being dyed from an acid bath and so allowing the simultaneous admixture of other acid dyestuffs to the bath. In distinction from alkali blue it is employed upon cotton mordanted with tannin together with alum, tartar emetic, or tin salt. Cotton is sometimes dyed directly from a bath containing some alum.

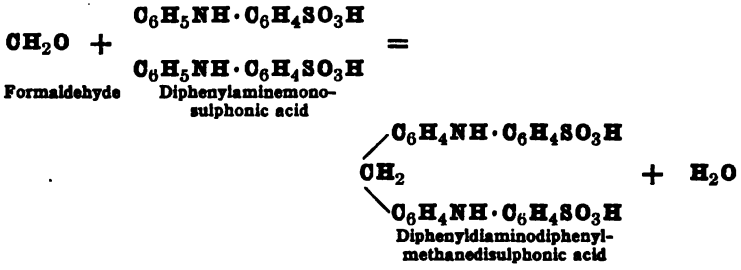
It is never used alone for dyeing silk and wool, as it is not so fast or so full as alkali blue.

Alcohol dissolves alkali blue and aniline blue from the dyed fabric in the cold while soluble blue resists even boiling alcohol.

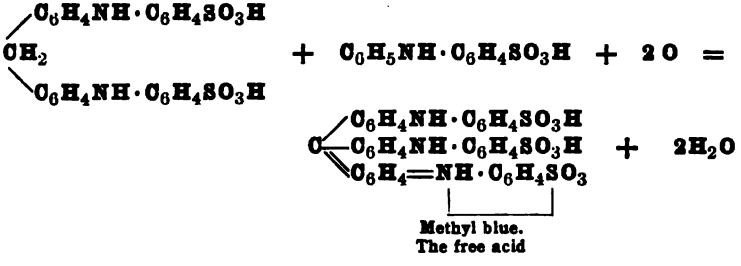
No change of color results when hydrochloric acid is added to its solution in water. A partial separation of the disulpho acid, however, as a blue precipitate takes place. The shade changes to a brownish red when caustic soda is added. The dark red solution in sulphuric acid becomes blue by adding water and a blue precipitate falls.

Methyl Blue (1862), Soluble Blue 8B., Soluble Blue 10B., Wool Blue, etc. From the previously mentioned dyestuff, soluble blue, this differs in purity and in manufacture. It is a trisulphonic acid of triphenylpararosaniline free from admixture with any rosaniline derivative.

Its most recent process of manufacture does not consist in the sulphonation of a previously prepared triphenylpararosaniline, but in using for combination components which have already been sulphonated. Thus, in the initial reaction, diphenylaminemonosulphonic acid and formaldehyde are brought together as follows:



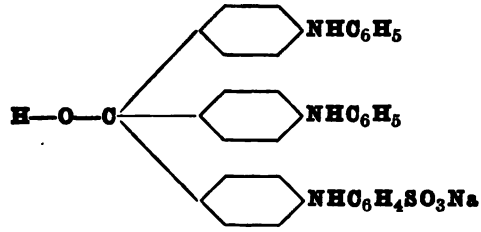
Oxidation of this product together with another molecule of diphenylaminemonosulphonic acid results, as shown below:


C6H4NH·C6H4SO3H CH2 C6H4NH·C6H4SO3H + C6H5NH·C6H4SO3H + 2O = C C6H4NH·C6H4SO3H C6H4NH·C6H4SO3H C6H4=NH·C6H4SO3 + 2H2O
Methyl blue.
The free acid

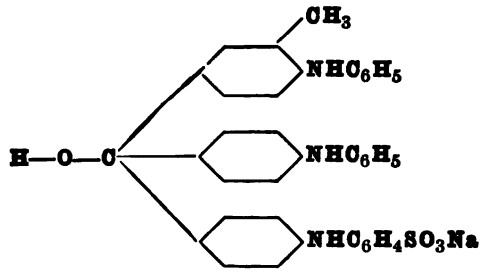
The disodium salt of this forms the commercial dyestuff. A variety of acid blue dyes are sold which are more or less pure trisulphonic acids of triphenylpararosaniline and rosaniline mixed with some mono- and disulphonic acid compounds.

A few among them are China blue, alkali blue, D. Bavarian blue D.S.F.

Alkali Blue (1862), Nicholson's Blue, Fast Blue. The action of sulphuric acid at 30–35° upon insoluble aniline blue is to convert it into a soluble monosulphonic acid, which is alkali blue. The resulting brownish yellow solution is poured into water and the new compound is precipitated. It is then washed and dissolved in the required amount of soda to form the sodium salt, which is the commercial form of the dye, and it is then obtained from the solution by salting out or evaporating to dryness, with the previous addition of a little carbonate of ammonia. The composition of the dye is shown in the following formula:



Alkali blue



Alkali blue

Alkali blue is a mixture of the sodium salts triphenylpararosanilinemonosulphonic acid and triphenylrosanilinemonosulphonic acid.

Alkali blue appears in commerce as a brownish powder or

in lumps which dissolve easily in about five times their weight of water. The aqueous solution is colorless; the addition of acetic acid in the cold causes a blue coloration, and on boiling, the free sulphonic acid is precipitated blue in color.

Hydrochloric acid completely precipitates the free sulphonic acid and the solution is left colorless if only a pure alkali blue were present. If, however, impurities in the form of di- and trisulphonic acids were present the liquid over the precipitate will remain colored. Any evolution of carbon dioxide is due to alkali carbonate present.

Sodium hydroxide changes its solution in water to a reddish brown. A beautiful brownish red color results on dissolving it in strong sulphuric acid; water causes a blue precipitate to separate.

Application. Dyeing with alkali blue is carried on in a weakly alkaline bath. It is especially adapted for bright shades on silk and wool but is not used for cotton, as it does not combine with acid mordants.

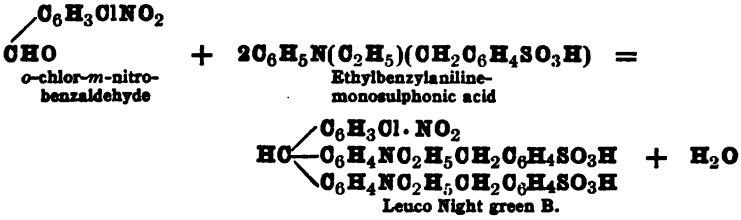
As lime salts form insoluble compounds with the dye, the water of the dyebath must be free from them or deprived of them by boiling with a little tin salt. The dyeing is carried on nearly at a boil, and to secure evenness and fastness borax or stannate of soda may be added to the bath.

A peculiarity of this dye over the other sulpho dyes is its ability to fix itself upon wool in a slightly alkaline bath in a colorless condition with no appearance of the blue color whatever. This property of the dye is ascribed to the basic amino groups present. In order to develop the blue color the goods are passed through a weak hot acid solution which converts the sodium salt into the free sulphonic acid which is the blue dye.

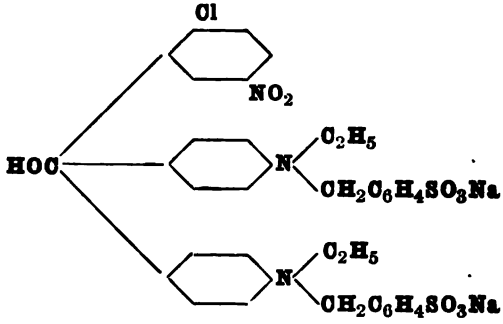
Night Green B. (1899) is an acid dye containing two sulpho groups which are fixed in the components before they are caused to unite.

Orthorchlor-*m*-nitrobenzaldehyde is caused to combine with

ethylbenzylaniline in the presence of some hydroscopic agent as follows:



Oxidation of this and the formation of the sodium salt produces the commercial dyestuff of a composition as follows:



Night green B.

A bluish green powder is the commercial form of the dye. It dissolves easily in water and alcohol to a bluish green color.

Hydrochloric acid causes a green precipitate and sodium hydroxide also produces a dirty green colored precipitate. Its yellow solution in strong sulphuric acid lets fall a yellowish green precipitate which slowly becomes bluish green on adding water.

Wool and silk are dyed a bluish green from an acid bath.

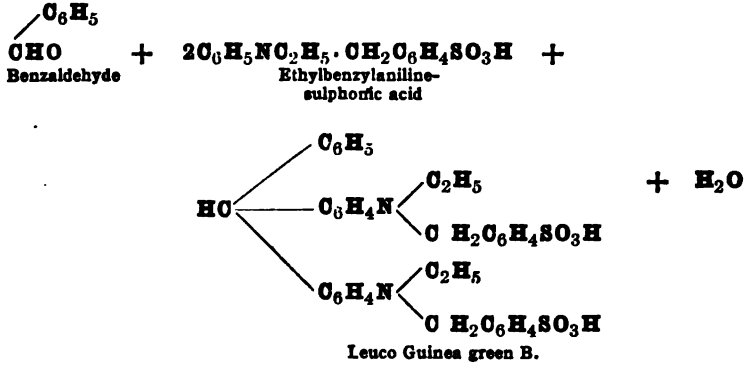
Night green 2B. differs from the above only in the lack of the nitro group NO_2. Its properties and uses are similar.

Guinea Green B. (1883) is an acid dye containing two sulpho and two amino groups and one of its three benzene rings without any modifying group.

The methane carbon is furnished by benzaldehyde, when, with zinc chloride to remove the water formed, it condenses with ethylbenzylanilinesulphonic acid,

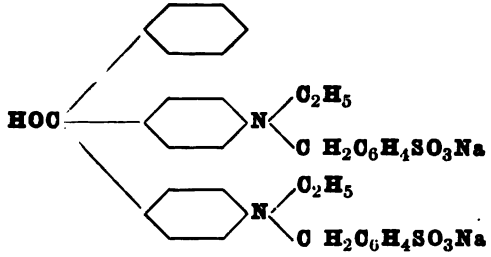
$$C_6H_5NC_2H_5 \cdot CH_2C_6H_4SO_3H.$$

The reaction runs as follows:



Leuco Guinea green B.

Oxidation of this product converts the methane group into a carbinol group and develops the properties of the dye. Then on neutralization with soda, the commercial dyestuff is obtained of the following composition:

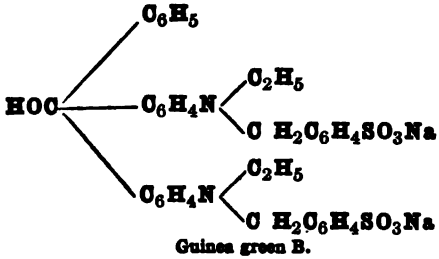


Guinea green B.

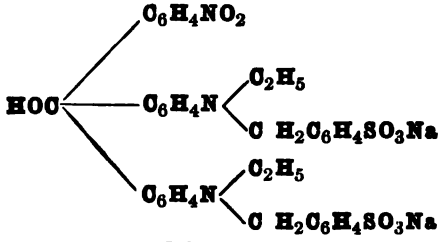
It will be noticed that one phenyl group contains no side group, but there is a dyestuff named Guinea green B.V., which possesses a nitro group in the meta position in this group in reference to the methane carbon. It is made in a similar manner to this dye by selecting a meta-nitrobenzalde-

hyde for the above condensation in place of simple benzaldehyde.

The difference which a single nitro group may cause in a dyestuff may be seen from the following comparisons:



Guinea green B.



Guinea green B. V.

	Guinea Green B	Guinea Green B. V.
Appearance.	Dull dark green powder.	Bluish green powder.
In alcohol.	Green solution.	Slightly soluble.
In water.	Green solution,	Green solution.
HCl to aqueous solution.	Brownish yellow.	Bluish green precipitate.
NaOH to aqueous solution.	Blackish green precipitate.	Light green almost decolorized.
H_2SO_4 Conc.	Yellow solution turning finally green on adding water.	Brown solution, turning finally yellowish green on adding water.
Dyes wool and silk from acid bath.	Green.	Green.

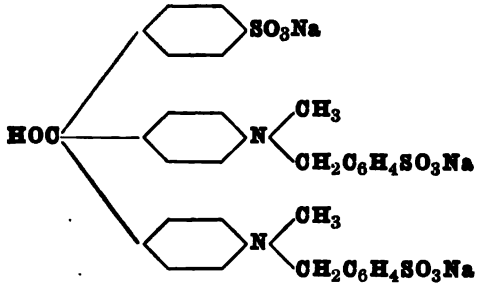
Both dyes are fugitive to light.

Guinea green B. is a dull dark green powder which dissolves easily with a green color in both water and alcohol. The blue aqueous solution is turned brownish yellow by hydrochloric acid. A dirty green precipitate falls on adding caustic soda. The yellow solution in strong sulphuric acid turns on adding water, yellowish red, yellowish green, and green in succession.

Light Green, S. F. Bluish (1879), Acid Green. This dyestuff differs in essential particulars from those previously

treated in this group. The methane carbon nucleus retains a hydroxyl group and consequently the dyestuff is a true carbinol. It is further a sulphonic acid (—SO_3H) derivative of a complex molecule; the effect of the entrance of the —SO_3H group into the molecule is to overcome the basic character residing in the amino groups and impart an acid character the molecule as a whole. The dyestuff is a true sulphonic acid and exhibits the color.

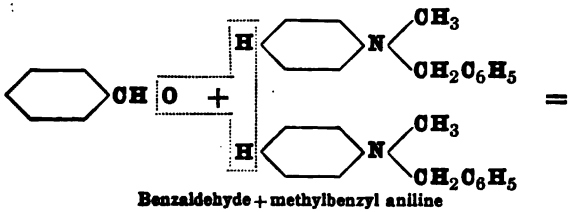
Light green S.F. bluish is prepared by the condensation of benzaldehyde with methylbenzylaniline, $C_6H_5N\begin{matrix}CH_3\\CH_2C_6H_5\end{matrix}$. This product is sulphonated, whereby sulphuric acid enforces the entrance of a sulphonic acid group into each one of the three benzene rings of the nucleus of this molecule. The result is the leuco base from which by oxidation the dyestuff is produced. Its completed structure is shown in the formula as a sodium salt of the dye:



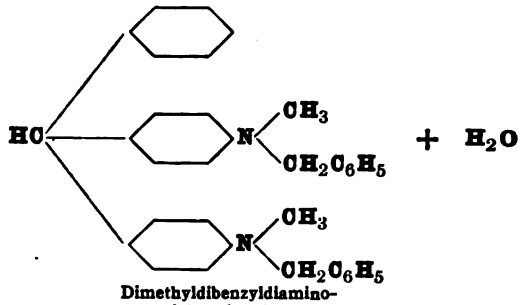
Sodium salt of light green S. F. bluish, or the sodium salt of dimethyldibenzyldiamino-triphenylcarbinol-trisulphonic acid

The commerical dye is in the form of a light green amorphous powder. It dissolves to a green solution in water. Wool and silk are dyed bright green with it from an acid bath. It is used to a large extent in conjunction with other acid shades for the production of compound shades on wool. Acid violet used with it produces various shades of peacock blue.

The condensation of benzaldehyde and methylbenzylaniline referred to above is here shown in detail:

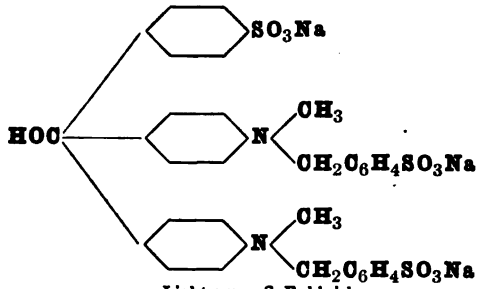


Benzaldehyde + methylbenzyl aniline



Dimethyldibenzyldiamino-triphenylmethane

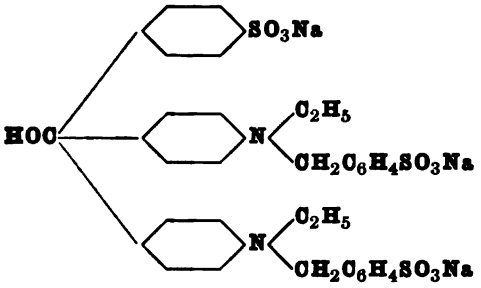
Sulphonation and oxidation then produces the dye:



Light green S. F. bluish

Light green S.F. bluish is a brownish black powder. Both water and alcohol dissolve it, forming green solutions. Hydrochloric acid turns the green aqueous solution yellowish brown. Caustic soda decolorizes it and causes a dirty violet cloudiness in its solution. The yellow solution in strong sulphuric acid is gradually changed to green on adding water.

Light Green S. F. Yellow Shade (1879). If in the above condensation, benzyl*ethyl*aniline had been used in place of benzyl*methyl*aniline then light green S.F. yellow shade would have been formed. This change from a bluish to a yellowish shade is therefore secured by substituting two ethyl groups for two methyl groups, no other change taking place.



Light green S. F. yellow shade

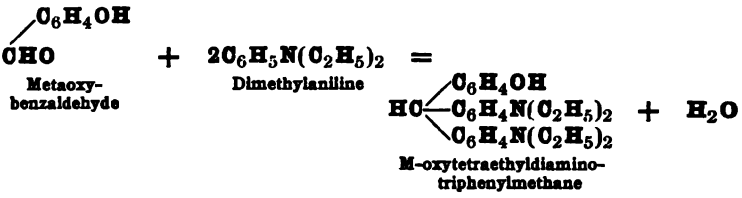
These dyes give the corresponding shades on wool and silk and they may be used in conjunction with other acid dyes for producing compound shades, e.g., with acid violet to develop a peacock blue.

Hydrochloric acid changes both greens to a yellowish brown color, while in both caustic soda gives a slight dirty violet precipitate.

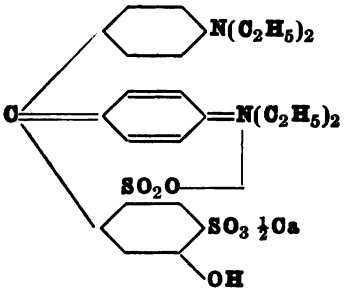
Patent Blues

Under this head are grouped a number of more recent dyes which possess unusual resistance to alkali, a valuable property in dyeing, and give pure shades of blue upon fabrics. They are disulphonic acids and yet they behave as monobasic acids. The theory of their fastness to alkalis will be discussed under the particular individual dyestuffs.

Patent Blue V.N. (1888), **New Patent Blue 4B.** is an acid dyestuff; a sulphonic acid derivative of oxytetraethyldiaminotriphenylmethane. One method of preparation starts with the condensation of metaoxybenzaldeyhde, HOC_6H_4CHO, and diethylaniline as follows:



By treatment with sulphuric acid, two sulpho groups are fixed in the molecule and the product neutralized to form the calcium salt: this by oxidation is converted into the dyestuff. The position of both the oxy groups and the sulpho groups is shown in the formula:



Patent blue V.N.

Formerly it was held that its peculiar fastness to alkali was due to the presence of the OH group, which is in a benzene ring in the meta position to the methane carbon atom; but later work has shown the improbability of this view, and from careful investigation it has been shown that a peculiar union of one of the sulpho groups with one of the amino groups of a neighboring benzene ring is responsible for its resistance to alkalis. This form of intramolecular combination is called the sultone formation. It causes the disulphonic compound to exhibit the properties of a monobasic acid.

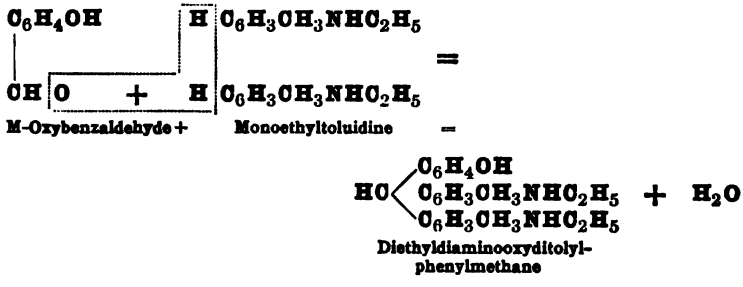
The dyestuff has the appearance of a copper red powder, which is easily soluble in water to a blue color and in alcohol with difficulty to the same blue color. Caustic soda does not affect it in the cold, but on boiling it turns violet.

Wool is dyed a greenish blue which equalizes well and is fast to alkalis and light. It is employed for mixed shades. Its greater fastness to light than that of indigo carmine has caused it to replace the latter very largely. In artificial light it shows a greener shade than by daylight.

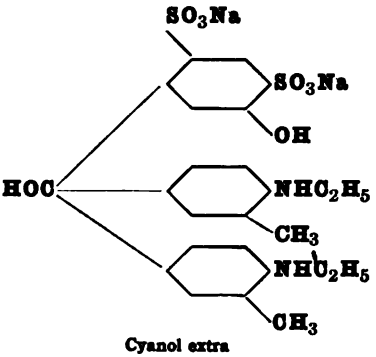
Patent Blue A. (1888) is a dye which is similiar to patent Blue V.N. in properties, constitution, and method of manufacture with this one exception, that instead of diethylaniline, $C_6H_5N(C_2H_5)_2$, which is a component of that dye, ethylbenzylaniline, $C_6H_4N(C_2H_5)CH_2C_6H_5$, is used. This produces a diethyldibenzyl compound instead of a tetraethyl compound, as in patent blue V.N.

Cyanol Extra (1891), **Acid Blue 6G.** is an acid dyestuff which owes its properties to the presence of two sulpho groups in the molecule. Were it not for these groups, it would exhibit the basic properties which reside in its amino groups and be classed among the basic dyes.

It is manufactured from metaoxybenzyldehyde, $C_6H_4OH \cdot CHO$, which is condensed with two molecules of monoethylorthotoluidine, $C_6H_4(CH_3)(NHC_2H_5)$, in the presence of some agent to take up water. The reaction runs thus:



On treating this product with sulphuric acid, two sulpho groups become fixed in that phenyl group which possesses the hydroxyl group: oxidation thrusts an oxygen into the methane group and this develops the color. The sodium salt, the form of the commercial dye, has the following composition:

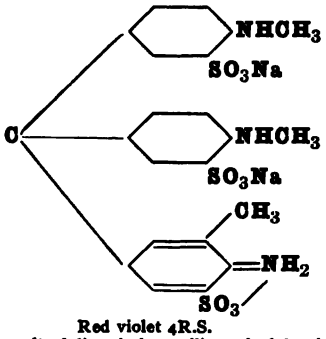


Cyanol extra

It is a dark blue powder which dissolves easily in water to a blue color.

Wool is dyed from an acid bath, and for wool it has largely displaced indigo carmine. Copper salts produce turbid effects and thus copper vessels should be avoided. It equalizes well in dyeing and is fast to washing, to light and alkalis, also moderately fast to milling.

Red Violet, 4R.S. (1877). If dimethylrosaniline is taken in place of rosaniline (magenta) for treatment with fuming sulphuric acid, a similar fixation of a sulphonic acid group results in each of the three phenyl groups. The product of such a sulphonation is red violet 4R.S. The dyestuff is a reddish violet powder. It dissolves easily in water with a magenta red color. It dyes a bluer shade than acid magenta on wool from an acid bath. The formula of its sodium salt appears below:

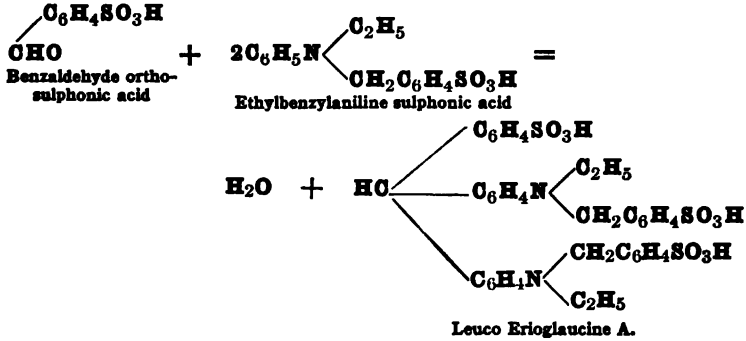


Red violet 4R.S.
(Sodium salt of dimethylrosaniline trisulphonic acid)

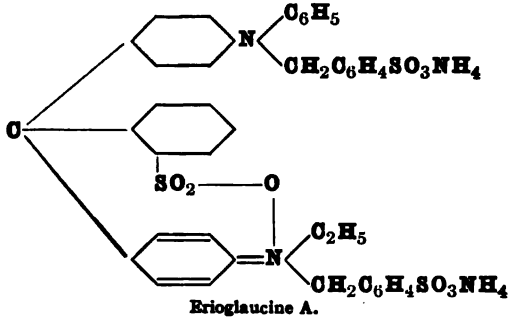
Hydrochloric acid produces no change in a solution of this dye. By warming with a solution of caustic soda, the color turns to a reddish yellow. Wool in an acid bath is dyed a somewhat bluer shade than with acid magenta. It is very sensitive to soda, ammonia, and street dirt of an alkaline character, while it is moderately fast to light and milling.

Erioglaucine A. (1896) is a blue dye containing three sulpho groups, one of which exhibits a sultone formation with an amino group in a neighboring benzene ring.

The components are already sulphonated when they are brought together. One molecule of benzaldehyde orthosulphonic acid is condensed with ethylbenzylaniline sulphonic acid, some hygroscopic agent assisting; the reaction is as follows:



This product is oxidized and a rearrangement takes place, developing a sultone union and also a quinone formation in different parts of the molecule, which is then neutralized to form the ammonium salt as shown below:

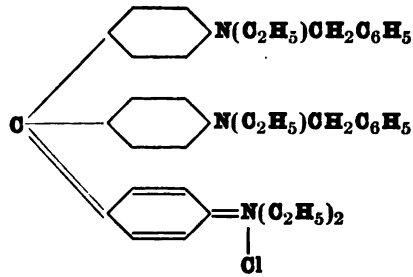


This is a dark blue powder in commerce, having a brown lustre. It dissolves easily with a greenish blue color in water and in alcohol. It is fast to alkalies, a property which is attributed to the restraining effect of the sultone union of the sulpho and amino groups. It dyes wool and silk greenish blue from an acid bath. Though sensitive to light, on account of its beauty, it is replacing indigo carmine.

Erioglaucine A. is a dark blue powder of a bronze lustre. It is soluble in water and alcohol alike with a greenish blue color.

Hydrochloric acid changes the aqueous solution to green and then causes the separation of a yellow precipitate. Caustic soda has no effect upon the cold solution, which, however, on boiling changes to violet. The pale yellow solution in strong sulphuric acid turns first green and then greenish blue as water is gradually added.

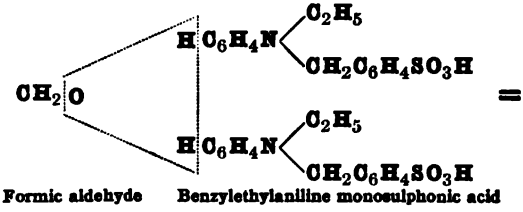
Acid Violet 6B. (1890). The basic dye methyl violet when treated with sulphuric acid becomes sulphonated by the entrance of (—SO_3H) groups and it is then an acid dye. Acid violet 6B. is a substance of complex composition; but as its nucleus there appears pararosaniline all of whose amino hydrogens have been replaced by four ethyl and two benzyl ($C_6H_5CH_2$—) groups. The resulting compound is a tetraethyldibenzylpararosaniline, the formula appearing as follows:



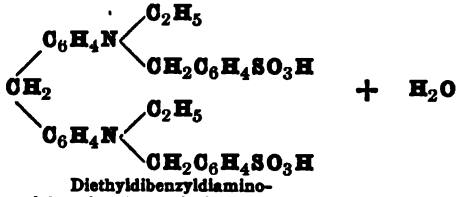
Tetraethyldibenzyl-pararosaniline hydrochloride

To convert this basic dye into an acid one, it is treated with sulphuric acid; but this treatment of a finished product is found difficult in practice. It is much easier to sulphonate the leuco compound and then oxidize the product to the dyestuff.

The manufacturing process actually used employs those substances to form the dye molecule which are already sulphonated. When benzylethylaniline monosulphonic acid is treated with formic aldehyde, a condensation results as follows:

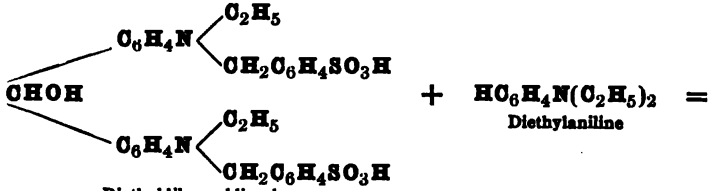


Formic aldehyde — Benzylethylaniline monosulphonic acid

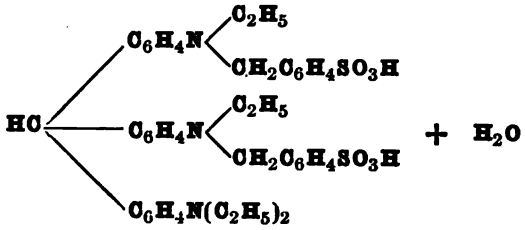


Diethyldibenzyldiamino-diphenylmethane disulphonic acid

By oxidation this product changes from a methane derivative to a hydrol: (=CH_2) becomes (=CHOH). The hydrol is then allowed to act upon diethylaniline as follows:

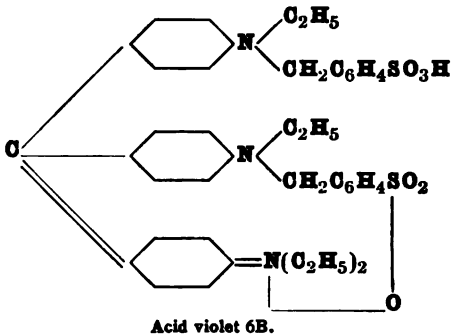


Diethyldibenzyldiamino-diphenylbenhydrol disulphonic acid



Tetraethyldibenzyldiamino-triphenylmethane disulphonic acid, or Tetraethyldibenzylleucaniline disulphonic acid

To develop the color of the dye, this product is oxidized and at the same time a salt-forming condensation takes place between an amino group and a sulphonic group with a result clearly shown in the following graphic formula:



Acid violet 6B.

Acid violet 6B. is a violet powder with a bronze lustre which dissolves in water with a bluish violet color.

Hydrochloric acid turns the solution yellow; then nearly colorless. Caustic soda causes a blue flocculent precipitate to form which loses its color on warming.

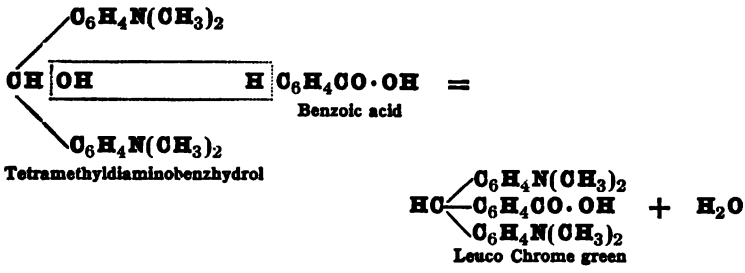
Strong sulphuric acid dissolves it with an orange color which turns, as water is gradually added, first olive green, then green, and finally blue.

Wool is dyed bluish violet from an acid bath. It equalizes well and it is adapted to production of mixed shades.

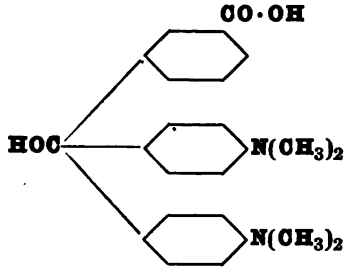
Silk is dyed a shade which is fast to washing.

Chrome Green (1891) takes its name from the chromium mordant with which it is used. It is an acid dye which owes its acid property not to a sulphonic acid, but to a carboxyl group. This latter group is brought into the reaction by one of the components which react to form the dye.

It is made by causing benzoic acid, $C_6H_5CO \cdot OH$, to condense with tetramethyldiaminobenzhydrol as follows:



This product is then oxidized to produce the dye by using the peroxide of lead.



From this formula it will be seen that the benzoic acid joins itself to the methane carbon so as to retain the acidifying group, —CO·OH, in the meta position.

Chrome green is a dark green powder which is soluble in alcohol and water to a greenish blue color. Hydrochloric acid yields a yellowish orange solution. Caustic alkali decolorizes it.

Wool which has been mordanted with chromium salts is colored a green which is not fast to light but fast to milling. It is employed chiefly for printing on cotton.

Chrome Violet (1891). If salicylic acid were substituted for benzoic acid in the previous dye, then it would introduce a hydroxyl group in a para position to the methane carbon, and this single addition to the chrome green changes it to chrome violet. It requires in dyeing a chromium mordant, and it is used principally in cotton printing.

Aurine (1834) is an acid dyestuff, and it is the oldest one from coal-tar, though it does not dispute the claim of Perkins

mauve, prepared more than twenty years later, to be the first artificial dye to be manufactured and sold.

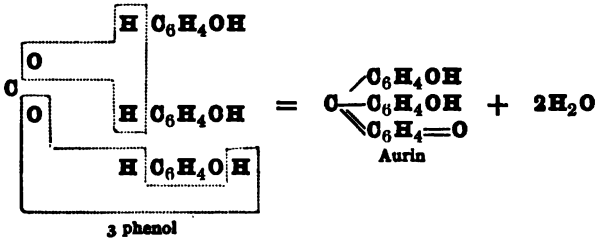
Runge observed in 1834 that a dye could be made from phenol and that it could form beautiful color lakes; but no attempt was made to put it to practical use.

Aurine is a mixture of related dyestuffs, and that component Runge is supposed to have made was rosolic acid. This dye, in contrast to those triphenylmethane dyes thus far studied, contains no nitrogen. It is an oxygen derivative of triphenlymethane.

The manufacture consists in heating 6 parts of phenol, 3 parts of sulphuric acid, and 4 parts of anhydrous oxalic acid for twenty-four hours at a temperature of 120–130°. After repeated extraction of the mass with boiling water, the residue is dissolved in hot alcohol, ammonia gas is conducted through the solution, and the resulting precipitate is boiled with acetic or hydrochloric acid. The dyestuff forms dark red rhombic crystals or shining greenish red needles.

It decomposes on heating before it melts. It is insoluble in water, but soluble in alcohol and glacial acetic acid, with a yellowish red color and with a rosaniline red color in alkalies.

The course of the reaction between the phenol and oxalic acid or rather the CO_2 from the oxalic acid is shown as follows:

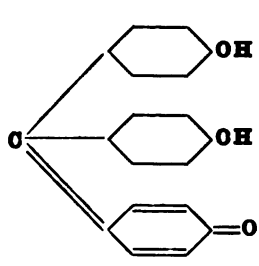


Reducing agents cause two atoms of hydrogen to become fixed in the molecule and also the change of the quinoid linking at the same time, so that leucaurine is formed which is a trioxytriphenyl methane.

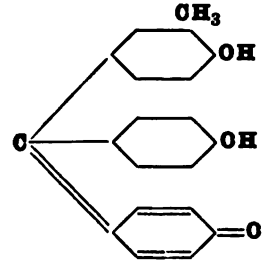
The intimate relation aurin bears to pararosaniline is shown by the fact that on heating with aqueous ammonia to 120°; it is converted into pararosaniline.

Aurin is used in staining paper and as a color lake for dyeing carpets; as a spirit lacquer it is applied to color tin-foil.

There is often a confusion of the two names aurine and rosolic acid; the latter is a methyl derivative of the former and results from employing methylphenol or cresol in place of phenol in its manufacture. The two following formulas clearly distinguish between them:



Aurine

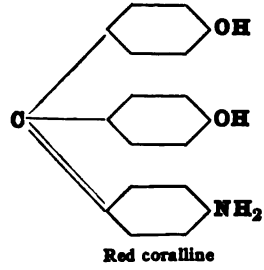


Rosolic acid

Yellow Corallin is the sodium salt of crude aurine.

Red Coralline contains nitrogen in the form of an amino group. This amino group is introduced into the molecule of aurin by heating it with ammonia and aniline. It was first prepared in Lyons in the early days of the coal-tar dye industry. Red coralline was for some time an important product in the market. It sometimes passed under the name peonine.

It probably consists of aurine with one or more of the hydroxyls replaced by amino groups, as shown in the formula.



Red coralline

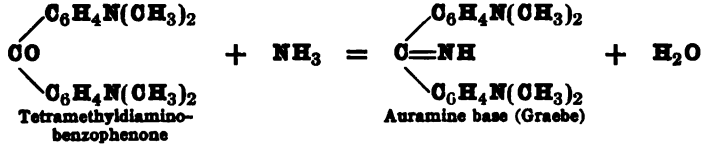
Its use has decreased, and is now employed to a limited extent to produce a bright red in cloth printing.

Diphenylmethane Dyes

Auramine (1883), Auramine O, takes its name from (aurum) gold. It is one of the very few basic yellow dyestuffs. When it was discovered by Cars and Kern, its importance was at once recognized as a basic tannin dyestuff for dyeing cotton and printing calico a yellow shade. As the dye lacks the fastness needed for calico and is decomposed by boiling water, it has not met the expectations that were first aroused. Still it is most extensively used of any of the basic yellow dyes, serving as a constituent of mixed dyes for cotton, and, as a sulphur-resisting dye for wool as well as for paper staining.

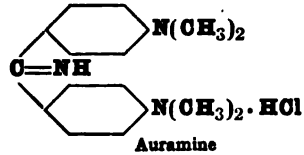
Among several methods of manufacture, the first one employed is most easily comprehended. It consists in heating tetramethyldiaminobenzophenone with ammonium chloride and zinc chloride for several hours to a temperature of 150–160°, agitation being kept up from time to time.

When a sample, withdrawn from the melt, dissolves in water the reaction is completed. The reaction is as follows:



Tetramethyldiamino-benzophenone — Auramine base (Graebe)

The cold melt is broken up and extracted with cold water, to which a little hydrochloric acid has been added, to remove any unchanged ammonium chloride or zinc chloride. By employing boiling water upon the residue, the dye is dissolved and after the solution is filtered, common salt is used to precipitate the dyestuff. It may be purified by recrystallizing from hot water. The commercial dye is the hydrochloride whose constitution is shown below:



Auramine

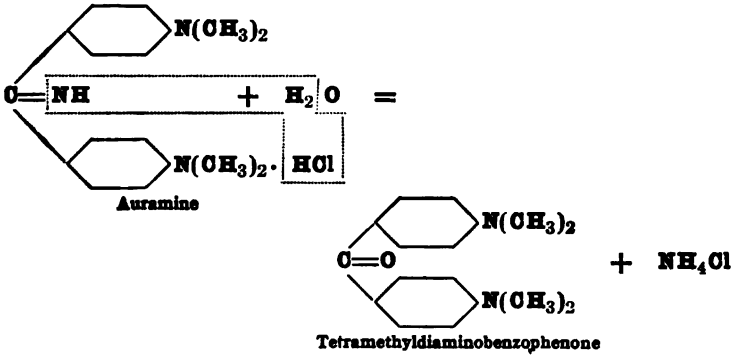
It is the hydrochloride of imidotetramethyldiaminodiphenylmethane. The sulphate and the acetate dissolve easily in water.

Mineral acids on standing with it for a considerable time, or on boiling, decolorize the solution decomposing the dye into its constituents ammonia and the original ketone base.

Auramine in commerce appears as a powder of a sulphur-yellow color. It dissolves with difficulty in cold water, but much more easily in water warmed to 70–80°, or by acidifying the water used to dissolve it. Alcohol also dissolves it.

Hydrochloric acid added to its aqueous solution causes any undissolved particles to dissolve at once. The solution turns a darker shade of yellow. On boiling the acid solution, the decomposition of the dye begins with the formation of ammonium chloride and tetramethyldiaminobenzophenone.

This decomposition of auramine in boiling water is shown as follows, whereby it forms the same substances which were used to make it:



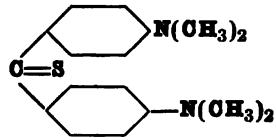
Caustic soda causes a white precipitate in the solution of the dye which will dissolve in ether. Acetic acid turns this ethereal solution yellow. The solution in strong sulphuric acid is without color, but the gradual addition of water restores it to a pale yellow shade.

Cotton which has been mordanted with tannin and tartar emetic is dyed yellow. From a neutral bath, wool and silk are dyed the same yellow color. Auramine is also employed

for coloring paper and leather, and it is still further of use in photography for producing yellow plates.

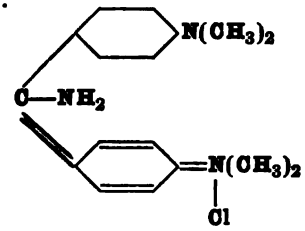
The present process of manufacturing the dye employs a method discovered by Sandmeyer in 1889. This involves the heating together of tetramethyldiaminodiphenylmethane, ammonium chloride, sulphur, and salt in a stream of ammonia gas.

A thioketone is first formed as an intermediate product. This thioketone is then transformed into auramine by the exchange of sulphur for the imino group and the union of hydrochloric acid with one of the amino groups, as shown below:



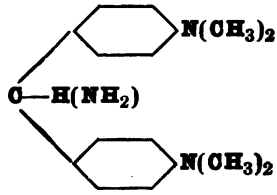
Thioketone

The formula of auramine given above has been written in a different manner by Stock, in which a quinone structure appears as follows:



Auramine (Stock)

By reduction, two atoms of hydrogen become fixed in the molecule of the yellow dye, changing it to the colorless base —the leuco base which on oxidation turns again into the original yellow:

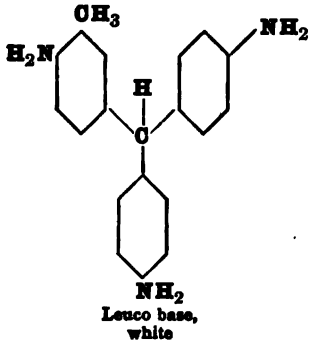


Leuco auramine

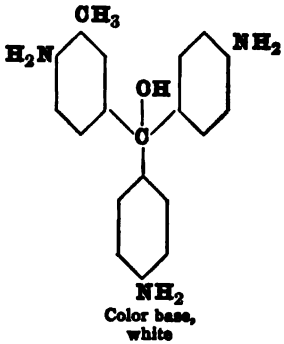
TABLE FOR COMPARISON

LEUCO BASE; COLOR BASE—THE DYE:

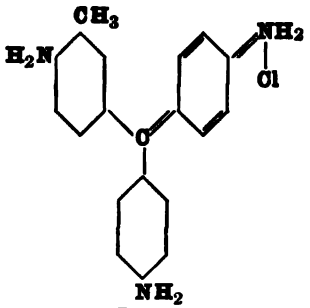
ROSANILINE



Leuco base, white

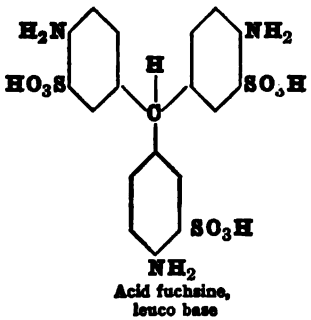


Color base, white

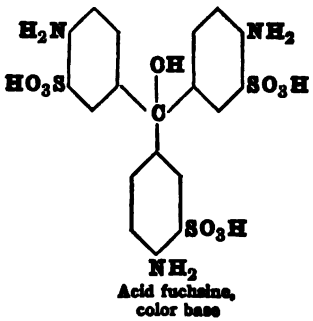


The dye: red

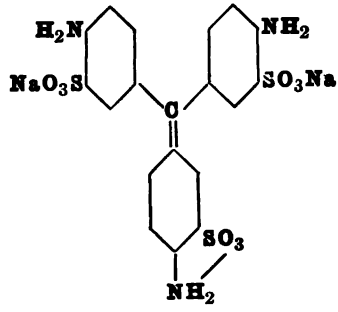
ACID FUCHSINE, OR ACID MAGENTA



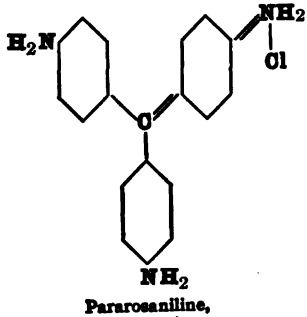
Acid fuchsine, leuco base



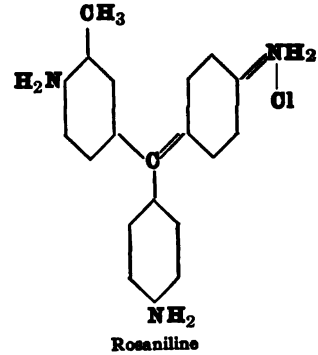
Acid fuchsine, color base



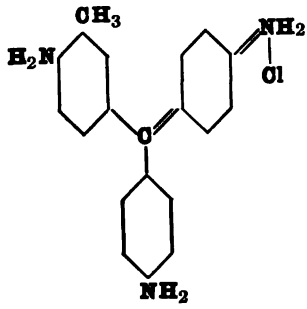
Acid fuchsine,
the dye: alkali salt



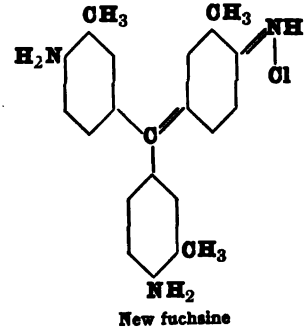
Pararosaniline,
parafuchsine



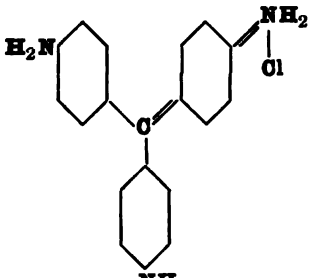
Rosaniline
fuchsine



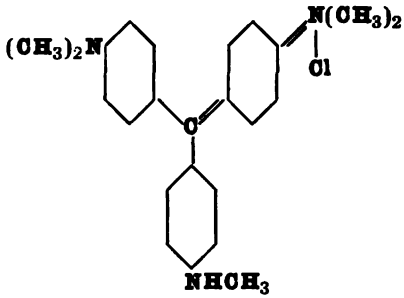
Rosaniline
fuchsine



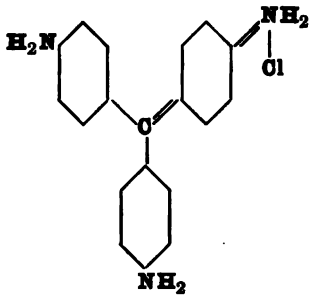
New fuchsine



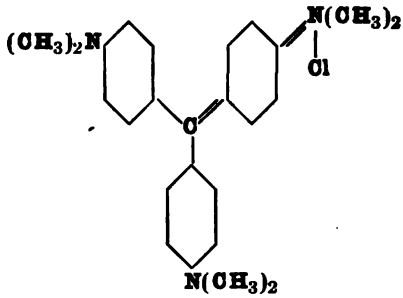
Para-rosaniline



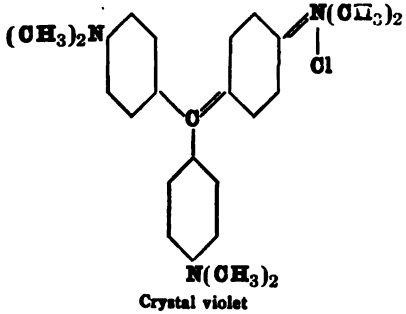
Methyl violet B. and 2B.



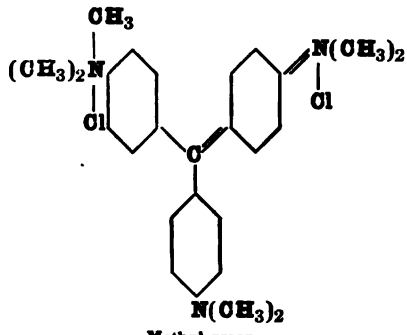
Pararosaniline



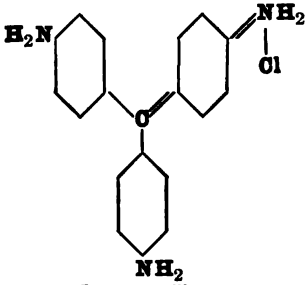
Crystal violet



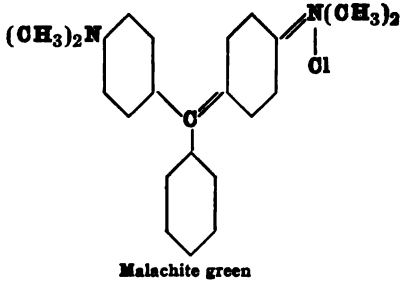
Crystal violet



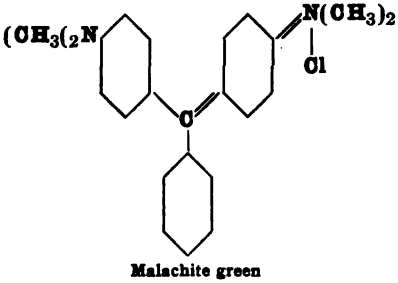
Methyl green



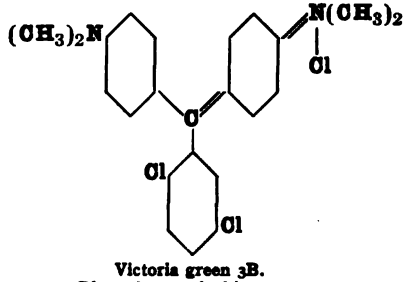
Para-rosaniline



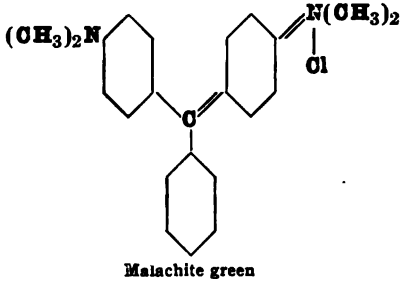
Malachite green



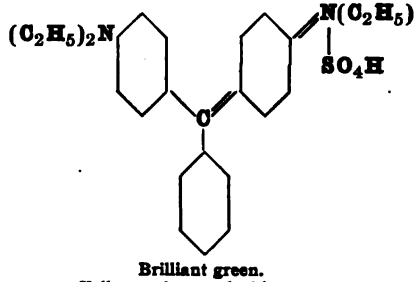
Malachite green



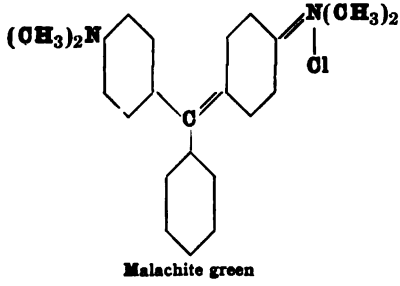
Victoria green 3B.
Bluer than malachite green



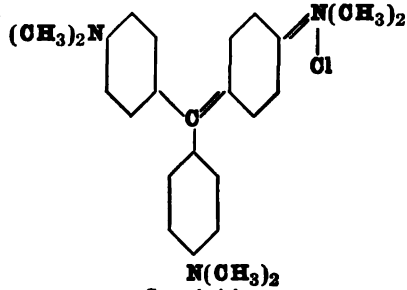
Malachite green



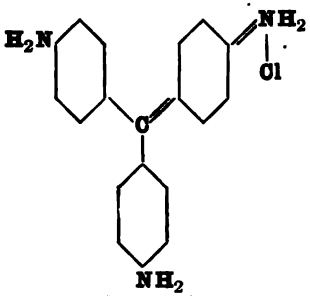
Brilliant green.
Yellower than malachite green



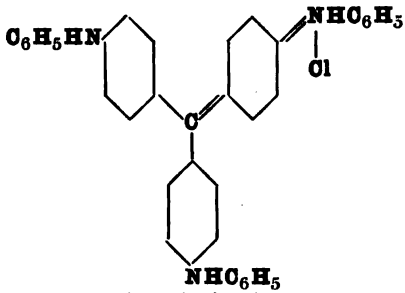
Malachite green



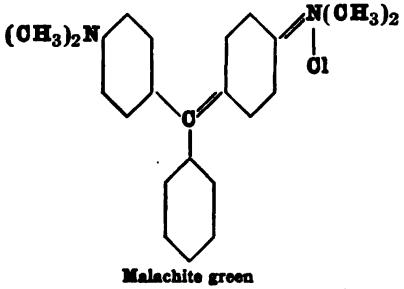
Crystal violet



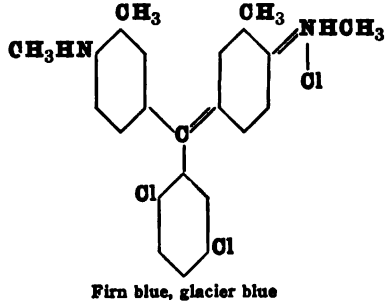
Pararosaniline



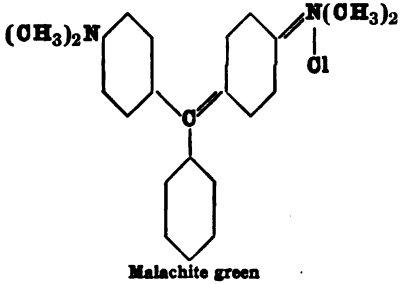
Diphenylamine blue
spirit blue, insoluble in water



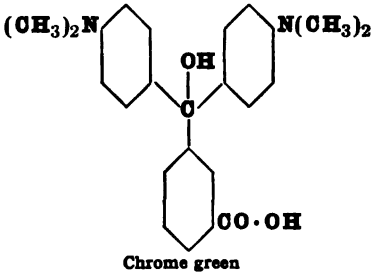
Malachite green



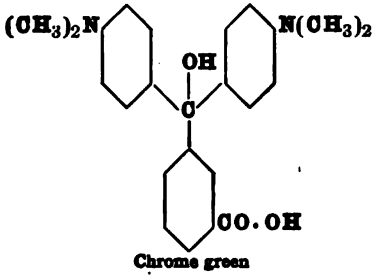
Firn blue, glacier blue



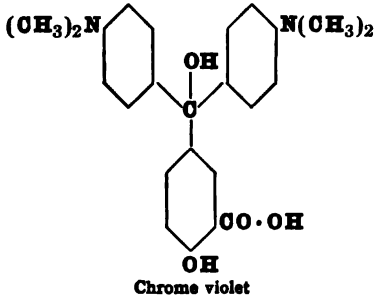
Malachite green



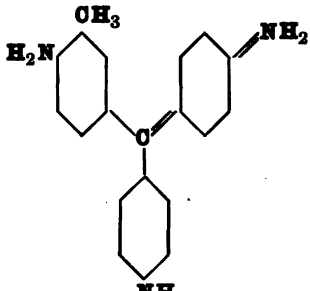
Chrome green



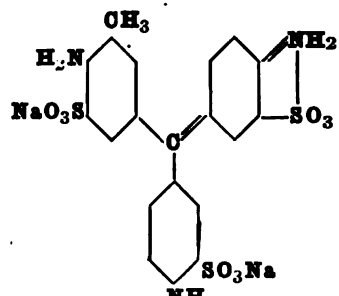
Chrome green



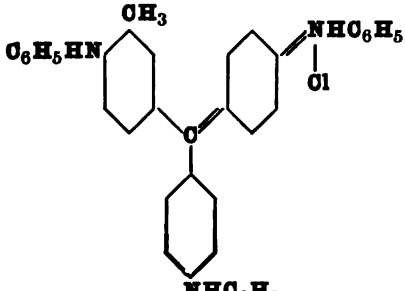
Chrome violet



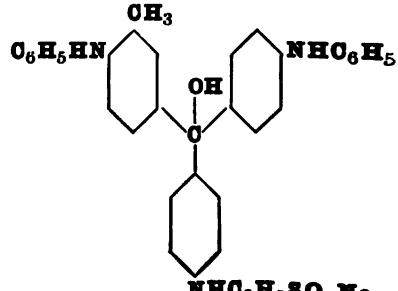
Fuchsine



Acid fuchsine



Aniline blue,
insoluble in water



Alkali blue,
soluble in water

CHAPTER VII

THE CLASSIFICATION OF THE COAL-TAR DYES

THE arranging of dyes into classes must naturally depend upon the differences and similarities which they exhibit. Since these differences and similarities will change if the point of view be changed, it follows that there may be several classifications, e.g., one based upon the source or origin of the dye; another upon the method of applying the dyes to fabrics; another one upon their chemical constitution, and so forth.

Classification by Source or Origin. From this point of view, the coal-tar dyes may be classed as, aniline dyes, naphthalene dyes, anthracene dyes, phenol dyes, etc. This arrangement is a confusing and useless one; because some dyes contain more than one of these substances.

Classification by Method of Application. This arrangement would be most useful from the point of view of the dyer, as the following eight classes will show:

1. **Acid Dyes.**
2. **Tannin Dyes.**
3. **Salt Dyes.**
4. **Sulphur Dyes.**
5. **Vat Dyes.**
6. **Mordant Dyes.**
7. **Developing Dyes.**
8. **Albumin Dyes.**

This exhibits to the dyer a tangible conception of why any particular dye must be used in the dye vat, whether it can be used alone, or must have some assisting substance also present in the solution of the dye; whether the goods

must be treated chemically before entering the vat or be exposed to air or other chemical treatment after leaving the vat; e.g.:

The Acid Dyes. The majority of these are sodium salts of sulphonic or carbon acids or nitro acids. Examples of these in order are the azo dyes, the eosines, and picric acid. Wool and silk are dyed directly with the aid of an acid or an acid salt in the bath. They are not suitable for dyeing cotton.

Tannin Dyes. These are also called basic dyes, and they are for the most part hydrochloric acid salts of color bases. Cotton, when first treated with tannin, is easily dyed, while silk and wool often take up the dye directly without any assistant.

Salt Dyes. Named from the neutral or alkaline salts which are dissolved in the solution of the dye. They are sometimes called direct-cotton dyes and substantive cotton dyes. The latter name is not wholly appropriate, for some of them are also very suitable for wool. The dyes are usually sodium salts of sulphonic or carbon acids and are taken up by the cotton fibre in this state. Common salt and Glauber's salt are used at the same time in the bath.

Sulphur Dyes. This is a class of colors which have come to the front of late years on account of the cheapness and fastness of their dyeings. They produce fast shades on cotton from a bath made alkaline with the soluble sulphides. The development of the color usually requires oxidation after the material is removed from the bath.

Vat Dyes. These dyes are indifferent in their chemical behavior and show no attraction for the common fibres. They can only be fixed upon the material by being reduced to their leuco compounds in the vat; the material to be dyed is then immersed and becomes saturated with the reduced dye, for which it shows a real affinity. Then, by removal, the color is developed by subsequent oxidation on exposure to the air. Indigo blue is an example of this class.

Mordant Dyes. These dyes possess a weakly acid character and exhibit no attraction for the fibres. They become dyes

only when united to certain substances called mordants, with which the fabrics are impregnated before entering the dye bath.

Alizarine is such a dye; it is a yellow and almost insoluble substance which, when boiled with cotton previously treated with aluminum salts and Turkey red oil, and afterward with calcium salt, produces the celebrated Turkey red.

Developing Dyes. The developing dyes are insoluble and hence as such cannot be applied to the textile fibres. They are produced upon the fibre itself by saturating it with one soluble component and then immersing it in a bath of another soluble component, when these components unite to form an insoluble dyestuff fast in the substance of the fibres. Paranitraniline red is produced in this manner.

Albumin Dyes. Require some strongly adhesive substance upon the fibre before the dyes will be taken up. Albumin is frequently used for this purpose. Many of the mineral pigments and color lakes have been employed in this way.

The division of dyes, as shown in the above grouping, reveals little or nothing of the chemical constitution of the molecules of the various dyes. An attempt to classify the dyes upon the basis of similar chemical constitution originated with Graebe and Liebermann in 1867, based upon the conversion of dyes into leuco compounds by the action of nascent hydrogen. Little resulted from this; but in 1876 Otto N. Witt proposed a more adequate theory of the constitution of the dyes.

In his investigations he reached conclusions which may be stated as follows:

1. In every dye molecule there is a certain group of atoms which has an especially powerful influence in making the substance a dye, and as he regarded it as the necessary color-giving group, he called it the "**Chromophore.**"

2. When this chromophore enters into combination with, or may be found as part of a larger molecule, this larger molecule is called a "**Chromogen.**"

3. The chromogen is not a dye, but it becomes a dye upon the entrance into the molecule of such groups as will give

it the power of forming salts. These groups are called "**Auxochromes,**" or color assistants, e.g., OH or NH_2.

We may select aminoazobenzene to illustrate the scope of these three terms.

$$C_6H_5—N=N—C_6H_4NH_2.$$
Aminoazobenzene

Here the chromophore is the azo group —N=N—; it has no separate existence and it never appears except as a constituent part of a larger molecule.

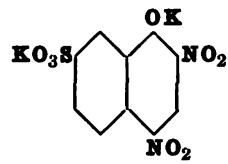
The chromogen is not the entire molecule of aminoazobenzene, but is all except the amino group, NH_2. The chromogen then would have the formula, $C_6H_5—N=N—C_6H_5$, and is called azobenzene.

The chromogen is an inert substance, and is not a dye. It has no power to form salts with either acids or bases.

This power is conferred upon it by the entrance of an auxochromous group, (—NH_2), to form a basic substance or a hydroxyl group (—OH), to form an acid one. In this instance, the amino group, on entering the chromogen, converts it into a basic substance which can form salts with acid that will dissolve in water and is available as a dye. The formula of the hydrochloric acid salt, formerly appearing in commerce as a dye, is:

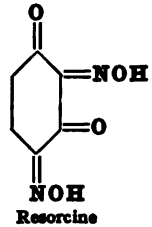
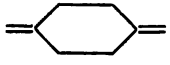
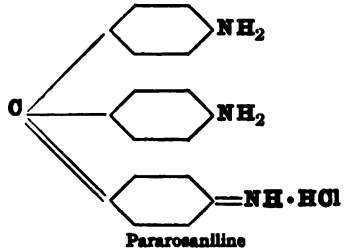
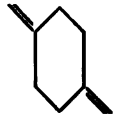
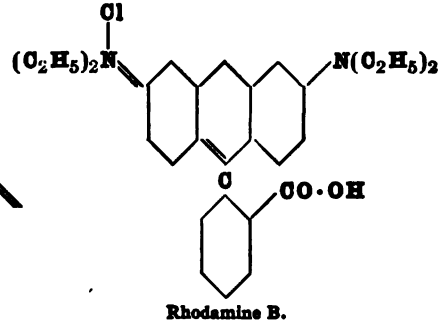
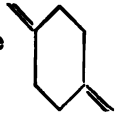
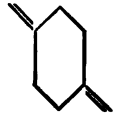
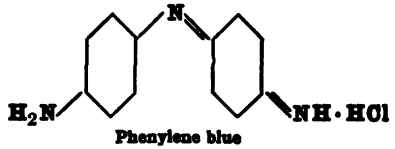
$$C_6H_5—N=N—C_6H_4NH_2 \cdot HCl$$
Aminoazobenzene hydrochloride

In the following list appear the chromophore groups as they have been worked out for several classes of dyes, and their positions are shown in the dye molecules given as types.

Name of Dye.	Chromophore.	Type of Dye.
1. Nitro Dyes	—NO_2*	

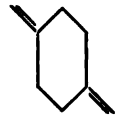
Naphthol yellow S.

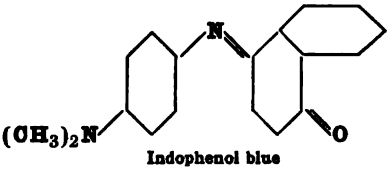
* The nitro group is no longer regarded as a chromophore.

Name of Dye.	Chromophore	Type of Dye.
2. Nitroso Dyes		 Resorcine
3. Triphenyl-methane Dyes		 Pararosaniline
4. Pyronine Dyes		 Rhodamine B.
5. Diphenylamine Dyes		
a. Indamines		 Phenylene blue

Name of Dye.	Chromophore.	Type of Dye.

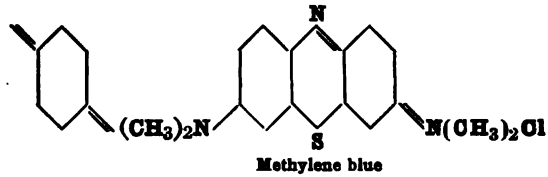
b. Indophenols





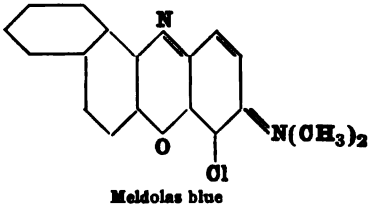
Indophenol blue

c. Thiazines



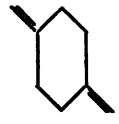
Methylene blue

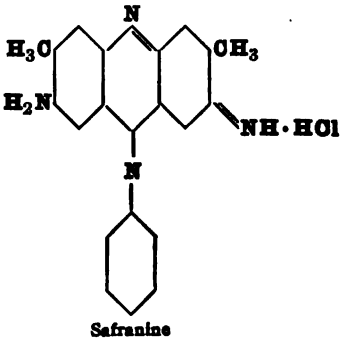
d. Oxazines



Meldolas blue

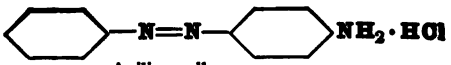
e. Safranines





Safranine

6. Azo dyes —N=N—



Aniline yellow

CHAPTER VIII

THE AZO DYES

This class of dyes takes its name from the word "azote," the French for nitrogen, not only because the element nitrogen is present in every one of the dyes, but because it is present as a double nitrogen atom or group called the azo group. This peculiar group consists of two atoms of nitrogen bound to each other by two valences, while two free valences, one to each nitrogen atom, thus

$$—N{=}N—$$

are left for the attachment of other atoms or groups. In its formation the azo group is not produced alone, but it is always developed from a single amino group of some primary amine, e.g., aniline by the action of nitrous acid, which furnishes the second nitrogen atom of the group.

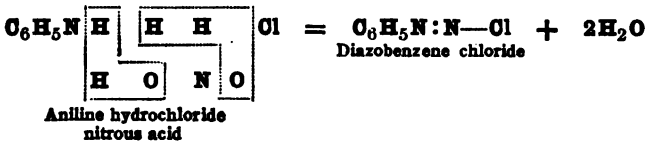
Diazo Compounds

As preliminary in every instance to the production of an azo dye, a diazo compound must first be formed, this class of bodies will be briefly discussed. In their composition, they possess the azo group —N=N—, as well as the true azo dyes afterward developed from them.

When nitrous fumes (N_2O_3 from nitric acid and starch or arsenious oxide) are passed into a cold acid solution of an aniline salt, e.g., the chloride, the following representative action takes place:

$$As_2O_3 + 2HNO_3 = \underset{\text{Nitrous anhydride}}{N_2O_3} + As_2O_5 + H_2O$$

$$N_2O_3 + H_2O = 2HONO$$



This process of converting amino into diazo compounds is known as diazotizing, and the products are diazo compounds, in this instance diazo benzene, and as the free acid present immediately combines with it to form a salt, the final product of this particular reaction is diazobenzene chloride.

In practice the nitrous fumes are not produced outside and then conducted into the solution; but the nitrous acid is formed directly in the cold acid solution of the amino compound by the addition of sodium nitrite, which immediately decomposes by aid of the mineral acid present and furnishes the required diazotizing agent. The substances are used in the molecular proportions indicated in the following reaction:

$$\underset{\text{Aniline hydrochloride}}{C_6H_5NH_2 \cdot HCl} + HCl + NaNO_2 = C_6H_5N:N—Cl + NaCl + 2H_2O$$

Diazobenzene chloride

The reaction is quantitative and it is one of the most easily controlled of any of the reactions of color manufacture. It is carried on at the present time upon an enormous scale.

If in the above reaction nitric or sulphuric acid had been used to dissolve the aniline and also to a calculated excess, then, on adding the sodium nitrite, the corresponding salts of diazo benzene would have been formed. Their formulas are:

Diazobenzene nitrate, $C_6H_5N:N—NO_3$

Diazobenzene sulphate, $C_6H_5N:N—SO_4H$

The diazo compounds are the starting points of the azo compounds.

The diazo benzene salts or the diazo salts, as they are called, are in general very unstable bodies, and if allowed to dry are in danger of spontaneous explosion. Even if the cold solution in which they are formed is heated, the diazo compound decomposes, evolving all its nitrogen in fine bubbles rising through the liquid; while resinous products are formed, if the solution were neutral; but if free acid is present a phenol results, as represented by the following equation:

$$\underset{\substack{\text{Aniline}\\\text{hydrochloride}}}{C_6H_5N{:}NCl} + H_2O = \underset{\text{Phenol}}{C_6H_5OH} + HCl + N_2$$

The free diazo benzene, $C_6H_5N{:}NOH$, is so unstable that it decomposes at once on being separated from its salts.

The diazo compounds become more stable if electronegative groups are present in the benzene ring. Diazo nitrophenol, for example, may be preserved in the free state without undergoing decomposition.

The fact is, however, that diazo compounds are, in general, so unstable that their use in color manufacture would be largely prohibited if it were in practice necessary to prepare them in the dry state.

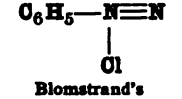
All danger of explosion or of slow decomposition may be avoided by preparing them in cold solution and then converting them into azo compounds, or dyes without isolation of the diazo substance in the dry state.

It may be stated, however, that in recent years, stable diazo compounds have been prepared which could safely be stored in the solid state. A patent process at Hochst on the Rhine consists in evaporating the strongly acid solutions of diazo compounds at 45° and mixing them with inert materials; or anhydrous aluminum sulphate may be used to convert the concentrated diazo solution into the solid state. Other methods are used by different firms.

Constitution of Diazo Compounds

From what has been said above about the ease of carrying out the diazo reaction by nitrous acid acting upon a cold acid solution of a primary amine, it should not be inferred that the structure of diazobenzene and its derivatives has been or is even now settled beyond dispute. The structure of diazobenzene has been a subject of much discussion among chemists.

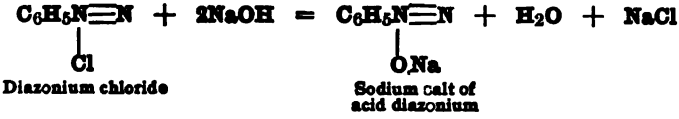
In place of the formula, $C_6H_5N:NCl$, by Kekulé for diazo benzene chloride, Blomstrand assumes a formula of the following character:



Blomstrand's diazobenzene chloride

From the fact that one of the nitrogen atoms exerts the same number of valences as it does in ammonium salts, this compound is called diazonium chloride. This formula is largely accepted as the typical structure and name of the diazo benzene salts, formed from acids.

When acted upon by alkalies, the diazonium compounds yield salts which exhibit them as having an acid function, thus:



Diazonium chloride

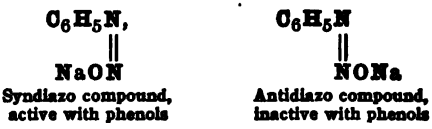
Sodium salt of acid diazonium

These alkali salts of acid diazonium can exist in two isomeric modifications: the first possesses the power to unite with phenols in alkaline solution and form azo dyes; but the second, obtained by more prolonged action of the alkali, at a higher temperature if requisite, does not manifest this property or only to a slight degree. Should the second form be treated with an acid it is changed back into the isomer which does unite with phenols to form azo dyes.

Bamberger ascribes the diazonium formula to the one active upon phenols and to the one inactive with phenols, the formula given below:

He regards the active form as the first product of alkalies upon the diazonium chloride, and the inactive form as a transformation from the first by the further action of the alkali.

Hantzsch, however, writes the formula for both alkali salts, $C_6H_5N:NONa$, but draws upon stereo-chemistry to explain the difference between the two as the following formulas show:



Bamberger holds a still different view and ascribes the formula, $C_6H_5N:N—OK$ to the active diazonium alkali salt and the phenyl nitrosamine formula, $C_6H_5NK—NO$, to the inactive alkali salt. By the action of acids even of atmospheric, CO_2, the inactive form changes into the active form which can produce azo dyes by acting upon phenols.

Bamberger and Hantszch both agree in accepting the diazonium formula of Blomstrand as the normal one for diazo benzene salts resulting from the action of nitrous acid on primary amines; but beyond this point appears divergence in their views and also in the opinions of other chemists.

In the following discussion of diazo compounds, as they relate to azo dyes, and in writing the formulas of the dyes themselves, the Kekulé constitution will be used for economy of space and from the uncertainty associated with the newer formulas.

The Azo Compounds

Though the diazo compounds, which form the basis of the azo dye manufacture, were discovered by Peter Griess in 1858, the first fifteen years passed with little fruit of this epoch-making discovery. Aniline yellow was discovered in 1861 by Mêne and a year later by Griess, and in 1863 Bismarck brown: little further was accomplished for more than a decade.

One reason for this lack of progress was the incorrect notion that the diazo compounds had to be separated from the solution in which they were formed before combining it with an amine or phenol to produce the dye.

The manufacture of the diazo compound and the coupling with a necessary component form one of the easiest and simplest operations of the dye manufacture.

The addition of sodium nitrite to an acid solution of an amine during diazotization is easily controlled by placing a drop of the solution upon iodostarch paper, which, when any excess of free nitrous acid is present, shows a blue stain at once, indicating a sufficient addition of nitrite.

For an easier understanding of the azo dyes, they are arranged in groups.

Basic Azo Dyes

Aniline Yellow (1861). The number of basic azo dyes is small, and aniline yellow is numbered among them. It is produced by coupling diazobenzene chloride with aniline; but, at first, the result is diazoaminobenzene, which must then undergo a transformation to produce the dye.

The reaction at first carried out is the following:

$$\underset{\text{Diazobenzene chloride}}{C_6H_5—N:N—Cl} + \underset{\text{Aniline}}{C_6H_5NH_2} = \underset{\text{Diazoaminobenzene}}{C_6H_5—N:N—NHC_6H_5} + HCl$$

A molecular rearrangement of the latter portion of this substance takes place upon gentle warming with aniline chloride:

$$C_6H_5N{:}N{-}\boxed{NHC_6H_5 + H}C_6H_4NH_2HCl =$$

Diazoaminobenzene — Aniline chloride

$$C_6H_5N{:}N{-}C_6H_4NH_2 \cdot HCl + C_6H_5NH_2$$

Aminoazobenzene chloride or aniline yellow

The probable course of this molecular readjustment is that the =NH group of diazoamino compound unites with a hydrogen atom of the benzene ring in the aniline chloride; thus a molecule of aniline which was coupled by its amino group is eliminated and there is joined in its place an aniline molecule which is coupled by its benzene ring, and places its amino group in the para position to the azo group. Theoretically, a very small amount of aniline chloride would suffice for the conversion of a large amount of diazoaminobenzene; but, in practice, different proportions are employed.

On a manufacturing scale the process is carried out as follows: To the aniline taken, only so much hydrochloric acid and sodium nitrite are added as will convert one-third of the aniline into diazoaminobenzene, and this product remains dissolved in the excess of aniline present. The hydrochloric acid must have been so calculated that, after the decomposition of sodium nitrite, some aniline chloride will be present for the second phase of the reaction, which requires gentle warming.

When the reaction is complete, the excess of aniline is dissolved in dilute hydrochloric acid and filtered off from the slightly soluble aniline yellow.

The chloride is the commercial form of the dye, which exhibits needle-like crystals of a bluish violet color with a bright lustre. It is insoluble in water, but it dissolves in acid solutions with a fine red color. On warming this solution the salt is decomposed and the free base is precipitated; it may also be effected by adding ammonia to a solution of its salts.

In the pure state, the free base forms yellow crystals, insoluble in water but soluble in alcohol.

If silk is placed in acid solution of aniline yellow, the reddish color is absorbed, the dye being taken into the silk in the form of the salt itself, but on washing decomposition ensues and only the free base is fixed upon the fibre, dyeing it a yellow color.

Aniline yellow is used for coloring lacquers, but on account of its fugitive character and its volatilization when steamed, it is not much used as a dye.

Its great importance depends upon its use as the initial substance in the manufacture of other valuable dyes.

Nascent hydrogen decomposes aniline yellow at the point of the double bond of the azo group with the formation of aniline and paraphenylenediamine as follows:

$$\underset{\text{Aniline yellow}}{C_6H_5N{:}NC_6H_4NH_2} + 4H = \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{p-Phenylenediamine}}{NH_2C_6H_4NH_2}$$

The azo group is the point of weakness of all azo compounds under the influence of reducing agents, and their easy disintegration serves as an important means of identification of the azo dyes.

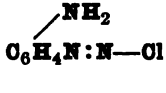
Butter Yellow (1875) is a dimethyl derivative of aniline yellow and results from coupling diazobenzene chloride with dimethyl aniline. It is not soluble in water, but it dissolves in oils. It is employed to color oils, butter, etc.:

$$\underset{\substack{\text{Butter yellow.}\\ \text{Dimethylaminoazobenzene}}}{C_6H_5{-}N{:}N{-}C_6H_4N(CH_3)_2}$$

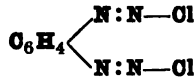
Bismarck Brown (1863), **Vesuvine, Phenylene Brown, Manchester Brown, Leather Brown, Cinnamon Brown, English Brown** is a mixture of two azo compounds; one containing one azo group, the other containing two.

Metaphenylenediamine, $C_6H_4\begin{matrix}NH_2\\NH_2\end{matrix}$, is diazotized with a double result. As there are two amino groups in the compound, either one or both may enter upon the diazo reaction.

As a matter of fact, part has one and part has each of the two diazotized. The results are as follows:

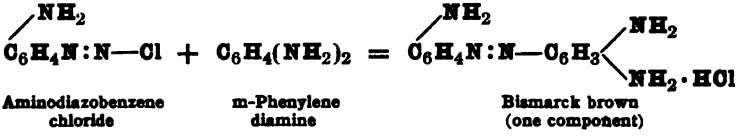


Aminodiazobenzene chloride

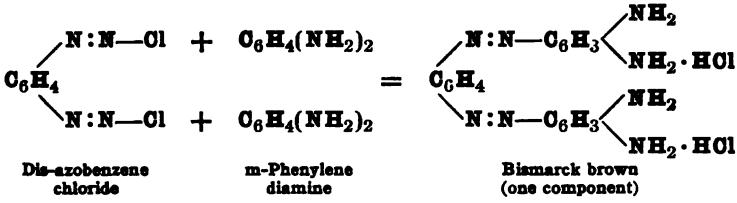


Dis-azobenzene chloride

The term dis-azo refers to the double azo group. It is evident that the first compound is in condition to become coupled with one molecule of metaphenylenediamine and the second with two such molecules:

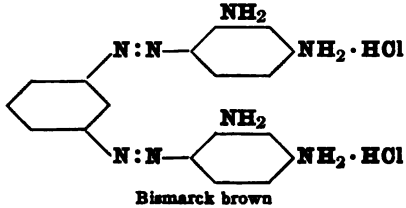


Aminodiazobenzene chloride — m-Phenylene diamine — Bismarck brown (one component)



Dis-azobenzene chloride — m-Phenylene diamine — Bismarck brown (one component)

The constitutional formula of the second component exhibits the position of the amino groups in the dyestuff:



Bismarck brown

It has been found that this latter constituent makes up the larger part of the commercial dye. In commerce, it appears as a brown powder which dissolves in water to a brown solution unaffected by hydrochloric acid. Caustic soda precipitates the brownish-colored free base. Reducing agents, e.g., stan-

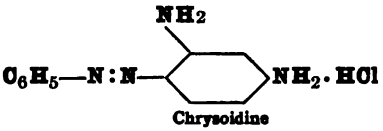
nous chloride and hydrochloric acid, decolorize it, causing a cleavage of the molecule at the double bonds of the azo groups.

Wool, leather, and tannin-mordanted cotton are dyed a reddish brown, which, however, is not fast to light or soap or milling.

Chrysoidine (1875) is of historical interest, for it was the first azo dyestuff to be prepared in the easier method of producing the dye in the same solution where the diazo compound is formed. It results from the mutual action of equivalent quantities of diazobenzene chloride and the chloride of *m*-phenylenediamine as follows:

$$\underset{\text{Diazobenzene chloride}}{C_6H_5N{:}N{-}Cl} + \underset{\text{m-Phenylenediamine}}{C_6H_4(NH_2)_2} = \underset{\text{Chrysoidine}}{C_6H_5N{:}N{-}C_6H_3\begin{matrix}NH_2\\NH_2HCl\end{matrix}}$$

Its constitution is exhibited in the following formula;



Chrysoidine

The dye appears either in large shining black crystals or as a reddish brown powder which dissolves in water to an orange yellow solution. From its aqueous solution, hydrochloric acid causes the separation of brownish yellow flocks which accumulate as a gelatinous precipitate.

Caustic soda causes the separation as a reddish brown precipitate of the chrysoidine base—diaminoazobenzene. It forms a brownish yellow solution in strong sulphuric acid which turns to cherry red as water is added.

Wool and silk may be dyed directly and cotton after mordanting with tannin an orange color. Its use is decreasing.

The Acid Azo Dyes

The majority of azo dyes are acid dyes, and they owe their acid properties either to the influence of sulpho groups, (—SO_3H), or to oxy groups, (—OH); occasionally a carboxyl group, (—CO·OH), may lend an acid character to the dye.

The influence of the sulpho group is to render the dye soluble but at the same time to lessen its affinity for the cotton fibre. In fixing a sulpho group in the molecule of a dye, concentrated or fuming sulphuric acid at varying temperatures may be allowed to act upon the ready formed substance; or the sulpho group may be already fixed in one or more of the components before they are coupled by the diazotizing process.

The position and number of the sulpho groups both have an influence upon the shade of the dye or upon its fastness to the various agencies that act upon it during its application to fabrics or those to which it may later be exposed while in use.

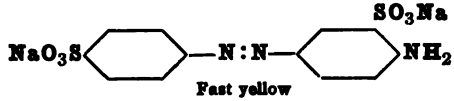
Then, further the sulpho groups are often present simultaneously with the oxy group or with the carboxyl group or with both.

Attention will be called to these effects of acid groups as the dyestuffs are described in detail.

Acid Yellow (1878), Fast Yellow G., Solid Yellow, New Yellow L. is a sodium salt of the disulphonic acid of aminoazobenzene mixed with some of the monosulphonic acid. The sulphonic acid groups are fixed in aminoazobenzene by the action of fuming sulphuric acid according to the following equation:

$$\underset{\text{Aminoazobenzene}}{C_6H_5—N:N—C_6H_4NH_2} + 2H_2SO_4 = \underset{\substack{\text{Aminoazobenzene}\\\text{disulphonic acid}}}{C_6H_4(SO_3H)—N:N—C_6H_3(SO_3H)NH_2} + 2H_2O$$

As a sodium salt, it forms the commercial dye, which is a yellow powder. The formula is as follows:



Fast yellow

Reducing agents decolorize it and act upon the central azo group, breaking the double bond and fixing two hydrogen

atoms upon each nitrogen atom. The molecule of fast yellow is thus resolved into sulphanilic acid upon the left side of the azo group and paraphenylenediamine sulphonic acid upon the right.

Fast yellow dissolves in water to a yellow color, but with difficulty in alcohol.

Hydrochloric acid produces two apparently opposite effects in first forming a precipitate and then dissolving it. It first removes the sodium, setting free the sulphonic acid, which forms a reddish violet precipitate, then if more hydrochloric acid is added it unites with the amino group, forming a chloride which dissolves to a reddish orange solution.

Caustic alkali or ammonia does not affect it.

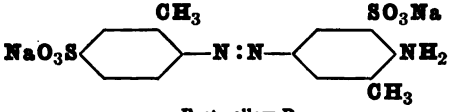
In strong sulphuric acid it forms a brownish yellow solution which turns to orange yellow as water is added.

It dyes wool and silk yellow in an acid bath. The dye is fast to light and milling. The shade obtained is almost a pure yellow, but not brilliant enough to be used alone, and it therefore serves for mixed shades. It may be used with acid rosaniline, indigo extract, and fast red. An excess of acid reddens the shade, and, when dyed upon a fabric, the shade is reddened by hydrochloric acid.

Large quantities of this dye are used for the manufacture of other diazo dyes.

Fast Yellow R. (1878), Yellow W., is the second higher homologue of the dye just described. It is the sodium salt of aminoazotoluene disulphonic acid.

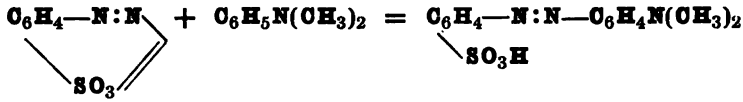
The formula is as follows:



Fast yellow R.

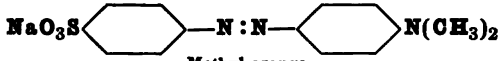
The presence of two methyl groups which this dye possesses over the fast yellow causes a deepening of the shade to a reddish yellow. Wool and silk are dyed reddish yellow from an acid bath.

Methyl Orange, Helianthine (1875), Orange III, Gold Orange, Tropæolin D., Dimethylaniline Orange. The starting point of this dye is paraaminobenzene sulphonic acid, $HO_3SC_6H_4NH_2$, which upon diazotizing becomes diazobenzene sulphonic acid. Dimethylaniline, $C_6H_4N(CH_3)_2$, combines with this as follows:



Diazobenzene sulphonic acid (anhydride) | Dimethyl-aniline | Methyl orange: free sulpho acid

The constitution of the commercial dye which is the sodium salt of the above compound is shown below:



Methyl orange

By comparing this formula with that of fast yellow R. it will be noticed that the two methyl groups in place of being fixed one in each benzene ring are here both contained in an amino group. This change of position deepens the shade of the dye from reddish yellow to orange, and it also strengthens the basic character of the amino group for the salts which this free base forms with acids are much more stable than those of simple aminoazobenzene, which are decomposable by water.

Methyl orange forms an orange yellow powder which yields a golden yellow solution in water. The coloring matter falls as an orange yellow precipitate on adding basic acetate of lead. Calcium chloride produces a precipitate of shimmering crystals, while solutions of salt or magnesium chloride causes the dyestuff to fall as such in minute crystals.

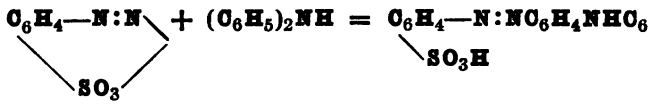
Slight amounts of acid cause it to turn red, and because of its sensitiveness in this respect it is often used as an indicator in volumetric analysis, possessing the advantage over phenolphthalein of not being affected by carbon dioxide or semi-combined sulphurous acid; thus it may be used for titrating carbonates and determining free sulphuric acid in sulphites.

Caustic alkali produces an orange yellow precipitate, but this dissolves in a large quantity of water.

Wool and silk are dyed orange from an acid bath. It is little used in dyeing, since it is fugitive to light and does not stand milling well. Almost its sole use is as an indicator.

Orange IV (1876), Tropæolin OO., Diphenyl Orange, Acid Yellow D., Orange G.S., is in many respects similar to methyl orange, but the difference is sufficient to cause its retention in dyeing while methyl orange finds almost its only use as an indicator.

Paradiazobenzene sulphonic acid is combined with diphenylamine, $(C_6H_5)_2NH$, according to the equation:



p-Diazobenzene sulphonic acid — Diphenylamine — Orange IV (free sulphonic acid)

The reacting substances are brought together in an acidified alcoholic solution.

Its constitution is shown below as its commercial form of a sodium salt:

Orange IV

This dye is a phenylated acid yellow; that is, one hydrogen in the amino group of acid yellow has been replaced by a phenyl group with a consequent increase in molecular weight and a change of shade from yellow to orange.

It is identical with methyl orange save that a phenyl group and a hydrogen atom exist here in place of two methyl groups of the methyl orange.

Orange IV appears in commerce as an orange yellow crystalline powder which is easily soluble in hot water, yielding an orange yellow color, but it is only slightly soluble in cold water or alcohol.

Hydrochloric acid turns the hot aqueous solution violet, and a voilet precipitate falls when the solution cools. Caustic

soda separates out a precipitate of an egg-yellow color. The violet solution in strong sulphuric acid lets fall a violet precipitate when water is added.

Wool and silk are dyed orange from an acid bath.

The dye upon the fabric is fast to light and milling and possesses strong coloring power. Though sensitive to acids, it is still used for wool and also for mixed shades.

Azo Yellow (1880), **Azoflavine, Indian Yellow, Citronine** are some of the names under which mixtures of nitrated derivatives of Orange IV appear in commerce.

If concentrated nitric acid is allowed to act upon Orange IV, a fixation of nitro groups takes place in the diphenylamine component of that dye.

Several advantages result from this enrichment of the molecule with nitro groups, the dye becomes less sensitive to acids, and is therefore of increased importance in wool dyeing, and the shade of Orange IV is thus more inclined toward yellow.

Metanil Yellow (1879), **Orange M. N., Victoria Yellow.** In this yellow dye may be observed the influence of a change in position of the sulpho group upon the character of a dye. The composition of this color is identical with that of Orange IV save that the sulpho group is fixed in a meta position to the azo group in place of a para position.

The preparation of the dye requires metaaminobenzene sulphonic acid, in which the position of the sulpho group is fixed before diazotizing and combining with diphenylamine.

The structure of both dyes is shown below:

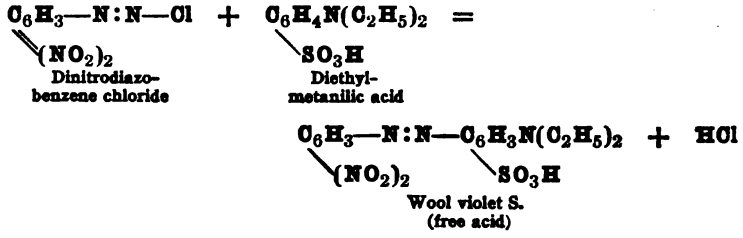
	Orange IV.	Metanil yellow.
Comparison.	Orange.	Yellowish orange.
Hydrochloric acid.	Violet precipitate,	Rosaniline red color and precipitate.
Caustic soda.	Yellow precipitate.	Unchanged.

Metanil yellow is employed more for wool than for silk, and it dyes an orange yellow from an acid bath. It is used for coloring both paper and lacquers. Though fast to light it is less so to acids.

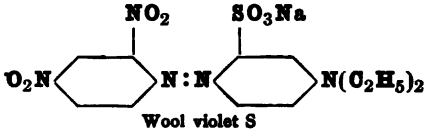
Wool Violet S. (1894). The prevailing colors of the monazo dyes—those possessing a single azo group—are the yellows and oranges. In wool violet S., there is, however, an example of a monazo dye whose color appears at the other end of the spectrum. It possesses both nitro and sulpho groups as well as a substituted amino group.

The starting point is dinitraniline, $C_6H_3(NH_2)(NO_2)_2$, which on being diazotized is coupled with diethylmetanilic acid, $C_6H_4N(C_2H_5)_2(SO_3)H$.

After diazotizing the reaction takes place as follows:



The dye appears as a blackish powder which is a sodium salt of the following constitution:



Wool is dyed a reddish violet from an acid bath.

Its lack, however, of resistance to acids which decompose the dye has caused its withdrawal from the market.

Oxy Azo Dyes

No class of dyes derived from the coal-tar products has won the attention or attained the importance of the oxy azo colors. In the last decade their manufacture has received a great impetus, and new products are constantly appearing upon the market.

The discovery of diazobenzol in 1860 made possible the enormous development of all the azo dyes; but, how great a

scope the diazo reaction comprised was not learned all at once. There were various periods of quiet which were changed into periods of enthusiastic investigation and technical activity when some new and untried substance was found available for diazotization or some new compound stood ready to form the second component and join with the diazo compound to produce a new color.

Ponceau Dyes

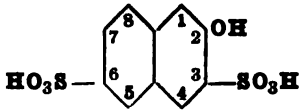
Among others, a group of dyes known as ponceau (poppy) dyes was discovered in 1878. They led the way for the production of the first scarlet dyes and similar compounds which are distinguished for beauty and cheapness.

The study of the methods of preparation of these dyes and a recognition of the different behavior of the naphthol disulphonic acids known as the R. and G. acids exerted a powerfully stimulating influence upon the synthetic preparation of dyes for a long time afterwards.

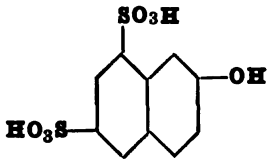
Typical substances used in the preparation of these dyes were the isomeric xylidines, $C_6H_3(CH_3)_2NH_2$, which were diazotized and united with the sodium salts in alkaline solution of the two β-naphthol disulphonic acids distinguished as the G. and R. acids.

In place of xylidine may be used cumidine, $C_6H_2(CH_3)_3NH_2$, and again other naphthol disulphonic acids may replace those above referred to.

The two acids referred to as R. and G. acids are both disulphonic acids of β-naphthol, and only differ from each other in the position occupied by one of the sulphonic acid groups. This difference in the position is important, and to recall the method of designating naphthol compounds the formulas are given below:



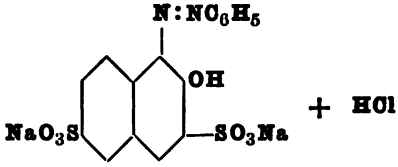
R-acid or β-Naphthol 3:6 disulpho acid



G-acid or β-Naphthol 6:8 disulpho acid

Ponceau 2G. (1878), Brilliant Ponceau G.G., Ponceau J.J., Scarlet 2G., is one of the first scarlet dyes. Aniline is the initial substance which is diazotized and coupled with β-naphthol disulphonic acid R. as follows:

$$\underset{\text{Diazobenzene chloride}}{C_6H_5:N:N—Cl} + \underset{\text{R-acid}}{C_{10}H_5OH(SO_3Na)_2} =$$

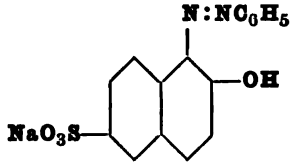


Ponceau 2G.

The dyestuff is a bright red powder, which gives a reddish yellow solution in water. It is scarcely changed by hydrochloric acid, but it is turned somewhat yellower by caustic soda. The cherry red solution it gives with strong sulphuric acid changes by adding water to reddish yellow.

Wool and silk are dyed from an acid bath a reddish orange color, which appears yellower under artificial light.

Ponceau 4G.B. (1878), Crociene Orange, Brilliant Orange, Orange G.R.X., differs from the preceding dye in composition only by the lack of one of the sulpho acid groups in the naphthol constituent of the dye. Its constitution is otherwise the same, as may be observed from the formula:



Ponceau 4G.B.

It is formed from diazotized aniline and β-naphthol sulpho acid S., containing the acid group in position 6.

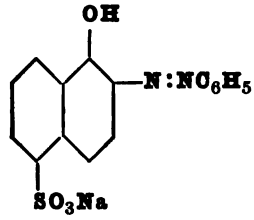
The loss of one sulphonic acid group in comparison with the previous dyestuff causes the color upon wool to incline

toward the yellow; it dyes an orange yellow, while ponceau 2G. dyes a reddish orange.

Hydrochloric acid causes a yellowish brown precipitate to fall. Besides dyeing wool from an acid bath it is employed in coloring lacquers. Its solution is turned brownish yellow by caustic soda. Strong sulphuric acid forms an orange yellow solution which gives a yellowish brown precipitate with addition of water.

Cochineal Scarlet G. (1883), is a monoacid dyestuff which exhibits the effect of a change in the position of the sulpho acid group in the molecule. This dye is an isomer of ponceau 4G.B., and differs from it only in having the single sulpho group in position 5 instead of in 6.

Comparison of the formula with the preceding clearly shows this.



Cochineal scarlet G.

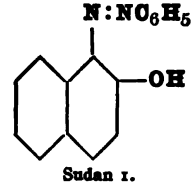
It is made from diazotized aniline and α-naphthol sulpho acid C.

The changed position of the sulpho group from position 6 to 5 changes the color from orange yellow to a brick red. It yields a red precipitate on adding hydrochloric acid. Caustic soda changes the aqueous solution to an orange yellow. Concentrated sulphuric acid dissolves it to a cherry red color which, as water is added, yields a brownish red precipitate.

Wool is dyed a brick red from an acid bath, and it is fast to light.

Sudan I (1883) is produced from diazotized aniline and β-naphthol. No sulpho acid group is present in the molecule. In this respect only it differs from the last named

dye, but from loss of this one acid group it is insoluble in water. Its composition is shown below:



Sudan I.

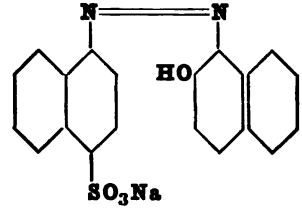
It is a brick red powder unfitted through its insolubility in water to serve as a dye for fabrics: it is used to color spirit lacquers and oils an orange yellow; waxes and soaps are likewise colored with it. It dissolves in concentrated acid, but it is insoluble in a solution of caustic soda. The red solution in strong sulphuric acid on dilution gives an orange yellow precipitate. It is soluble in benzene and its solution in this has been used in toning plush.

Fast Red A. (1877), Fast Red, Ceracine, Rubidine, Orcelline No. 4 possesses the distinction of being the first red azo dye, and it is likewise the cheapest among the red acid dyes.

Naphthionic acid, $C_{10}H_6(NH_2)SO_3H$, is diazotized and then combined with β-naphthol, which completes the formation of the dyestuff. The combination of the diazotized naphthionic acid with the second component is as follows:

$$\underset{\text{Diazonaphthalene supho acid}}{C_{10}H_6N:NCl(SO_3H)} + \underset{\beta\text{-Naphthol}}{C_{10}H_7OH} = \underset{\text{Fast red A.}}{C_{10}H_6N:NC_{10}H_6OH(SO_3H)} + HCl$$

The constitution of the dye is shown below in the form of its sodium salt, which appears in commerce:



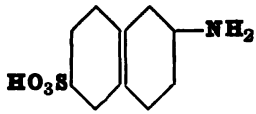
Fast red A.

The commercial dyestuff is a brownish red powder which dissolves slightly in cold, but easily in hot water, with a scarlet color. Hydrochloric acid gives a brown precipitate in this solution, while caustic soda turns it darker in color. A violet colored solution is formed with strong sulphuric acid from which a yellowish brown precipitate falls on adding water.

Fast red A. possesses strong coloring power and it produces a red color on wool dyed from an acid bath. It is also used for silk and but little for cotton.

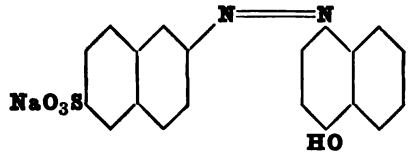
Its fastness to light and milling and its resistance to dilute acids and alkalies are the causes of its retention to the present time.

Fast Brown 3B. For the starting point of this dye there is required a sulpho acid compound of β-naphthylamine, which has the acid group in the position 6, as shown here:



β-Naphthylamine-6-sulpho acid

When this compound has been diazotized it couples with β-naphthol for a second component, forming the dye fast brown 3B, which dye is here represented as the sodium salt that appears in commerce:

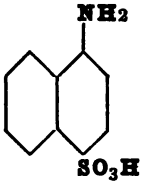


Fast brown 3B.

The dye is sold as a brown powder which gives a brownish red solution in water. Hydrochloric acid turns the color to reddish violet and a rosaniline red color is developed by caustic soda. The blue solution in strong sulphuric acid turns to a reddish violet as soon as water is added and then deposits a precipitate.

Wool is dyed brown from an acid bath and the color is moderately fast to light and milling; it also resists the action of acids and alkalics.

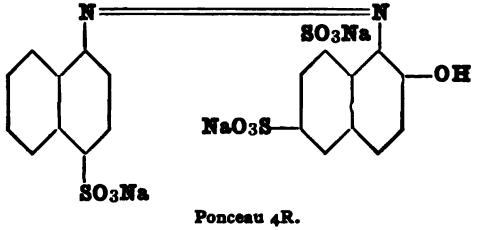
Ponceau 4R. (1878), New Coccin, Brilliant Scarlet, Cochineal Red A. This dye contains, like so many of the azo colors, two derivatives of naphthalene joined together by the azo group. The initial component is naphthionic acid or 1-4-naphthylamine sulpho acid of the following composition.



Naphthionic acid

Diazotizing its amino group enables it to fix one molecule of β-naphthol disulpho acid by attaching itself to position 1 in that molecule.

As the following formula exhibits the completed dye as the sodium salt of commerce, the second or more complicated component may be seen in the second part of the whole molecule.



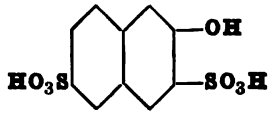
Ponceau 4R.

It forms a scarlet powder which dissolves in water with the same color. Hydrochloric acid does not change it; but it is turned brown by caustic soda. Strong sulphuric acid dissolves it with a rosaniline color, which dilution with water changes to yellowish red.

Wool and silk are dyed scarlet from an acid bath and the color is not at all affected by light; the color on the fabric resists well the action of alkalies and acids.

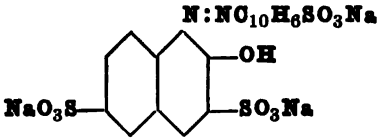
Bordeaux S. (1878), Fast Red D., Amaranth, Fast Red E. B. has the same empirical formula as the last named dye Ponceau 4R., but a different structure, and it allows a comparison therefore of the differing shades of the two isomers. Both are red dyes, the former a scarlet red and the latter a bluish red.

The initial component of both dyes is the same naphthionic acid, but Bordeaux S. results from employing R. acid in place of the G. acid to unite with the diazotized naphthionic acid.



β-Naphthol disulpho acid or R-acid

The R. acid is attached at position 1 to the diazotized naphthionic acid. The commercial dye is a sodium salt represented below:



Bordeaux S.

By comparing the formula of this with that of its isomer ponceau 4R. the only difference consists in the —SO_3H group having the position 3 in this dye in place of position 8, but this change develops a bluish character in the scarlet red of ponceau 4R.

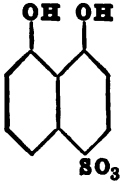
Bordeaux S. is a brownish red powder which gives a rosaniline red color to water. It is not changed by hydrochloric acid, but caustic soda turns it dark. It forms a violet solution in strong sulphuric acid and this only changes to a bluish violet upon diluting it.

It has the property of equalizing well in dyeing. Wool and silk from an acid bath are dyed a bluish red and this color is not sensitive to acids or alkalies. It is fast to light.

Azofuchsine G. (1889) is employed for bottoming indigo dyeings, and it is further used for mixed shades on cashmeres.

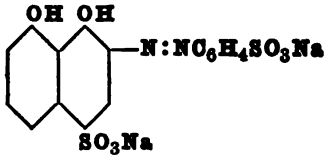
There are also other azofuchsine dyes which impart rosaniline shades to wool.

It is prepared by diazotizing *p*-sulphanilic acid, $C_6H_4NH_2SO_3H$, and uniting to it dioxynaphthalene sulpho acids of this formula:



Dioxynaphthalene sulpho acid S.

The resulting compound appears in commerce as a sodium salt of the composition:

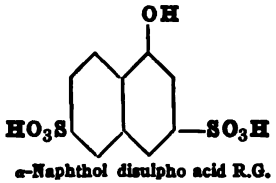


Azofuchsine G.

It is a reddish brown powder which imparts a bluish red color to its aqueous solution. Hydrochloric acid turns it bluer and caustic soda yellow without any precipitation.

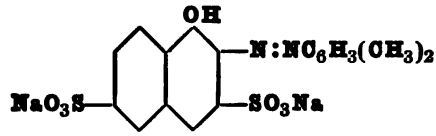
It dyes wool a rosaniline red from an acid bath and the color is fast to light and acids and moderately fast to alkalies and milling.

Palatine Scarlet (1886), Cochineal Scarlet P. S. The amino group required for diazotizing in the preparation of this dye is furnished by *m*-xylidine, $C_6H_3(CH_3)_2NH_2$. The second component is α-naphthol disulpho acid R.G., and has the constitution shown below:



α-Naphthol disulpho acid R.G.

The point where coupling with the diazo compound takes place is at position 2, and the result of the union is given as the commercial sodium salt:



Palatine scarlet

The dyestuff is a brownish red powder which dissolves easily in both water and alcohol with a scarlet color.

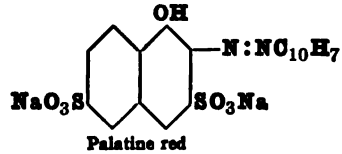
A gelatinous yellowish brown precipitate falls on adding hydrochloric acid, while caustic soda changes the color to yellow.

From an acid bath, wool is dyed scarlet. It is highly prized for its fastness to light and further distinguished by fastness to milling and the influence of sulphur.

The color is not sensitive to the action of acids and alkalies.

By referring to the formula of ponceau 2R., it will be observed this dye is an isomer. The difference consists in the exchange of position of the hydroxyl and diazo groups, but this change is accompanied by a loss of resistance to light; for ponceau 2R. is fugitive on exposure.

Palatine Red is similar to Palatine scarlet just described, but it differs in having a naphthyl group, $-C_{10}H_7$, in the place of a xylidine radical. This change in composition is accompanied by a change of color from scarlet to red.



Palatine red

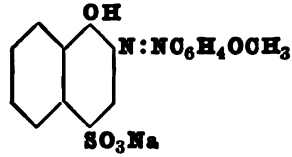
Diazo α-naphthylamine plus α-naphthol disulpho acid R.G. produces the dye whose sodium salt is represented.

The properties of the dye are almost identical with palatine scarlet. Wool is dyed a bluish shade of red. The color possesses resisting qualities against alkalies and sulphur. It is also fast to light to a considerable degree.

Azoeosine (1883) is a dye especially for wool, to which it

communicates a beautiful eosine red color. The amino group for diazotizing is furnished by *o*-anisidin, $C_6H_4NH_2(OCH_3)$. After the diazo compound is prepared it is joined to α-naphthol sulpho acid N. W., $C_{10}H_6SO_3H(OH)$.

The commercial dye is the sodium salt, the structure of which is exhibited in the formula:



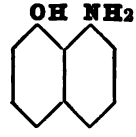
Azoeosine

It is a red powder which dissolves in water with a red color. A brown precipitate is thrown down by hydrochloric acid. Caustic soda turns the color to a yellowish brown. The carmine red solution in strong sulphuric acid lets fall a brownish red precipitate on the addition of water.

In an acid bath, wool is dyed an eosine red.

Lanacyl Violet B.—Among the monoazo dyes thus far considered the colors have been largely among the yellows, oranges, and reds and their various shades. It was discovered, however, that a certain kind of naphthalene derivatives used as a component would produce the darker colors, and under the proper conditions black.

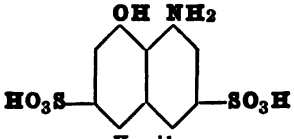
Lanacyl violet B. is one of these. The positions 1 and 8 in naphthalene are known as peri or neighboring positions. A dioxynaphthalene 1:8 would be a peri compound: an amino-α-naphthol 1:8 would also be a peri derivative with an amino group, (—NH_2), in position 1 and an oxy group, (—OH), in position 8 of the composition:



Amino-α-naphthol, 1:8

The disulpho acid of this compound with the sulpho groups in the position 8 and 6 is what is employed in the preparation

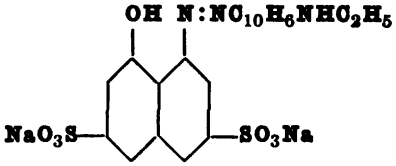
of lanacyl violet, and it is called H. acid of the following composition:



H. acid,
1-Amino-8-α-naphthol
3:6-disulpho acid

The capability of producing a dark color seems to reside in the positions assumed by the amino and oxy groups.

When subjected to diazotization and combined with ethyl α-naphthylamine, $C_{10}H_7NH_2H_5$, the violet dye is developed. The sodium salt is exhibited below:

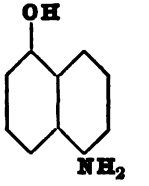


Lanacyl violet B.

It is a dark brown powder whose aqueous solution is reddish violet. Hydrochloric acid produces no change, while caustic soda turns it orange red. The solution in strong sulphuric acid is a greenish blue, which the addition of water turns first a greenish blue, then violet.

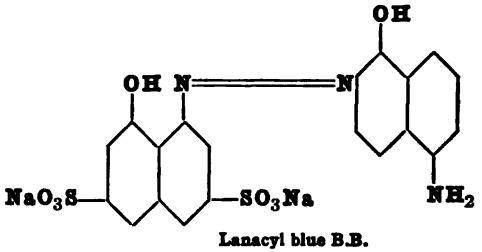
Wool from an acid bath is dyed a violet which stands milling and is fast to light and alkalies.

Lanacyl Blue B.B., resembles lanacyl voilet in requiring the same initial component, the H. acid; the second component is a naphthalene derivative also, but a different one. It is a 5-amino-1-naphthol, which for convenience in writing the formula of the dyestuff is represented in a reversed position:



5-Amino-1-naphthol

When the H. acid (see under Lanacyl violet) is diazotized and combined with the 5-amino-1-naphthol, the blue dye is produced, the sodium salt of which is:



Lanacyl blue B.B.

The dyestuff of commerce is a black powder which dissolves to a color between a red and a bluish violet. Hydrochloric acid produces slight effect; but caustic soda acts upon this as upon lanacyl violet, turning it an orange red. Strong sulphuric acid dissolves it with a blue color which the gradual addition of water does not affect at first, but it finally becomes violet.

Wool in an acid bath is dyed a blue which resists light well and is also fast to acids.

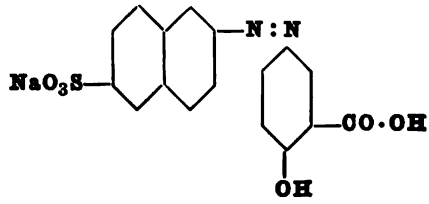
Chrome Yellow D. (1890), **Milling Yellow, Mordant Yellow, Anthracene Yellow B. N.** is an example of an azo dye requiring a mordant when dyed upon wool.

It differs from the other monoazo dyes in possessing a carboxyl group, (—CO·OH), and this gives a facility for combination with basic mordants, e.g., chromium hydroxide on wool.

β-Naphthylamine-6-sulpho acid is diazotized and combined with salicylic acid. It is this second component which communicates to the dye the property of combining with a chromium mordant.

Salicylic acid.

The sodium salt of the dye is



Chrome yellow D.

The yellow powder communicates a yellowish red color to its aqueous solution in which it is somewhat difficultly soluble.

A gray precipitate of a gelatinous character is thrown down by hydrochloric acid. An orange red precipitate falls on the addition of caustic soda. A flocculent reddish gray precipitate falls from its orange red solution in strong sulphuric acid as soon as sufficient water is added.

Wool that has been mordanted with bichromate of potash is dyed yellow. The color is fast to light and it stands milling. It resists acids and alkalies.

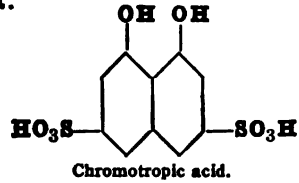
Chromotropes

The **chromotropes** form a group of dyes which take their name from "**chromotropic**" acid. They are manufactured at Hochst. A peculiarity of them is that being azo dyes, they nevertheless are mordant dyes. In practice the shade of the pure dye is modified to a greater or less degree by the mordant employed.

The dye is first applied and the mordant afterwards; thus it has the character of a developer and it is often called by that name.

The chromotropic acid which forms the basis of these dyes is a peri derivative of naphthalene and it is also a disulphonic acid and a dioxy compound at the same time. The two oxy groups are fixed in the positions 1 and 8, which are known as the peri positions. The compound is definitely expressed by the name 1.8-dioxynaphthalene-3.6 disulphonic acid, and the

relative positions of these four groups is shown in the constitutional formula:



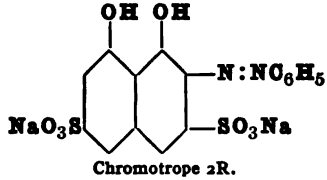
Chromotropic acid.

Position 2 in this acid is the point of fixation for any diazotized amine which can combine with it. The azo dyes which are thus developed by the various diazo components possess the property of being modified in hue by the different mordants used to fix the dyes. For instance, the dyestuff formed by coupling diazobenzene with this chromotropic acid yields, when dyed upon wool, a beautiful eosine red. If the wool be subjected to an alum mordant, the color changes to violet. When a chromium mordant is used a deep dark blue results.

The chromotrope azo dyes are mordant dyes; but they differ from other mordant dyes in the fact that wool is dyed from an acid bath and then the colored wool has the mordant applied by boiling in a solution of potassium bichromate (most frequently employed) until the desired shade is developed.

The three following chromotropic dyes show the effects produced upon the color of a dyestuff by the introduction of single simple groups, e.g., NO_2 and NH_2.

Chromotrope 2R. results from the combination of diazobenzene and chromotropic acid. The sodium salt is represented, showing the structure:



Chromotrope 2R.

It is a brownish red powder which colors water a rosaniline red. Neither hydrochloric acid or caustic soda affect the color.

Upon wool in an acid bath, it affords a rosaniline red which, by subsequent treatment with chromic acid, changes from a peacock blue to a very dark violet, according to the time of exposure to the action of the mordant.

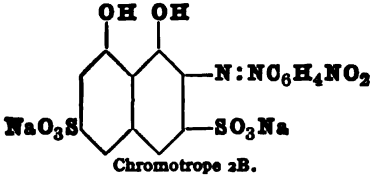
The color equalizes well, and it is very fast to light, acids, and the action of sulphur. It does not crock.

It is also moderately fast to alkalies, though not to milling. The range of its usefulness is increased by employing it for mixed shades.

By comparison with chromotrope 2B., next described, it will be noticed that the benzene ring, ($-C_6H_5$), contains no group substituted in place of any hydrogen.

Chromotrope 2B. (1890) is a mordant azo dye and a derivative of chromotropic acid. The other or first component is *p*-nitraniline, $C_6H_4NH_2(NO_2)$.

When this latter substance is diazotized and joined to the chromotropic acid, the dye is developed, and its commercial sodium salt is shown structurally as follows:



Chromotrope 2B.

The only change in composition from the previous dye, shown by this one, is the presence of one nitro group fixed in place of a hydrogen in the benzene ring.

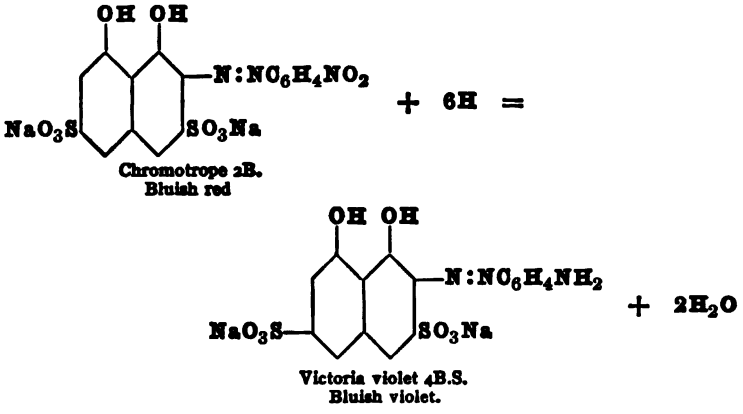
The presence of this group, however, changes the shade from red to a bluish red.

Chromotrope 2B. is a reddish brown powder yielding a yellowish red solution in water. Hydrochloric acid turns the color yellower and caustic soda turns it bluer. When dissolved in strong sulphuric acid, the solution is a dark violet color that changes on dilution to a yellowish red.

Wool is dyed various shades from an acid bath. It furnishes a bluish red when used alone: with a little potassium bichromate and acetic acid a blue, and with more bichromate and sulphuric acid a black color is developed.

Victoria Violet 4B.S. (1891) may well have been named a chromotrope dye, for it is derived from chromotropic acid. Indeed, it differs in no particular from chromotrope 2B. just described, save in the loss of two oxygen atoms from the single nitro group and their replacement by two hydrogen atoms.

As this loss of oxygen and gain of hydrogen is always the way in which reducing agents convert a nitro group into an amino group, so here this dye may be made directly from chromotrope 2B. by reducing agents.



Victoria Violet 4B.S. is a powder of grayish green color which forms a dark violet aqueous solution.

Neither hydrochloric acid or caustic soda causes a precipitate; but, the former turns it yellowish red, and the latter a reddish yellow.

Upon wool in an acid bath it dyes a bluish violet which is fast to washing and does not rub off. It is moderately fast to light and milling. A slight reddening of the color is effected by acids and alkalies.

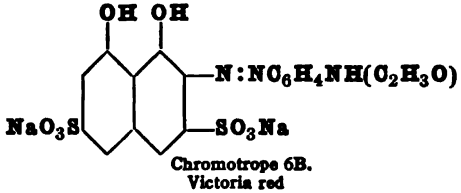
Chromotrope 6B. (1890) is a violet red dye which affords another example of a change in shade consequent upon a comparatively slight change in composition. This violet red dye may be considered as derivative of the bluish violet dye Victoria violet 4B.S., described above.

If this latter dyestuff should lose one hydrogen atom from its single amino group and gain in its place an acetyl, $-(C_2H_3O)$, group, the new dye would be formed.

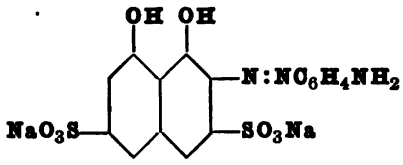
In the manufacture, however, the new dye is not obtained in this manner.

A component is chosen which already contains an acetyl group within the amino group. This component is *p*-amino-acetanilide, $C_6H_4NH_2NH(C_2H_3O)$.

It is diazotized and coupled with chromotropic acid, and the chromotrope 6B. results. The constitution of the sodium salt is:



Chromotrope 6B.
Victoria red



Victoria violet 4B.S.
Bluish violet

The fixation of the acetyl radical in the amino group has changed the predominant shade from violet to red.

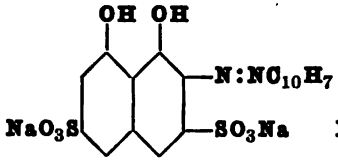
The commercial form of chromotrope 6B. is a grayish brown powder, whose aqueous solution is a violet red. It remains red with hydrochloric acid, but it is turned yellow by caustic soda.

Wool from an acid bath is dyed violet red. The dye equalizes well, and it is unaffected by light and acids. Alkalies have little effect upon it, but it lacks fastness to milling. Sulphur does not change it, nor does the color crock on rubbing.

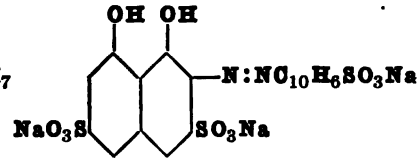
Chromotrope 10B. and Chromotrope 8B. are both reddish violet dyes which differ from each other by the one extra

sulpho group possessed by the latter dye. These two dyestuffs differ from the chromotropes previously considered in having naphthylamine as a starting point in place of aniline.

The constitutional formulas are:



Chromotrope 10B.
Reddish violet



Chromotrope 8B.
Reddish violet

By comparing the formula of chromotrope 8B. with that of chromotrope 2R., a naphthyl group, $-(C_{10}H_7)$, will be noticed in the former in place of a phenyl group, $-(C_6H_5)$, in the latter. This increase of molecular weight has changed the predominant red shade to a violet one, and this change from the lighter to the darker color will often accompany what may be called an increased molecular load, resulting from the introduction into a molecule of one or more heavy radicals.

Ingrain Colors

The term "ingrain colors" is applied to those colors which are actually formed or developed upon the fibre itself. The chemical reaction between the components of the ultimate color takes place upon the fibre. Iron buff is a simple example of an ingrain color among the inorganic dyes. A fabric steeped in a solution of a ferric salt shows little color until it is passed into a solution of an alkali or alkaline carbonate, when the ferric hydroxide develops, yielding a buff or brown color, according to the strength of the reacting substances.

All the azo dyes thus far considered, with the exception of a few basic dyes, are acid dyes, because of the contained sulpho acid groups. These sulpho groups render the otherwise insoluble dyes soluble, and thus capable of being dyed in the usual way from solution. A disadvantage of the sulpho group is the lessened affinity of the sulphonated dyestuff for cotton.

If the components of azo dyes are not sulphonated, then the resulting dye is insoluble and incapable of being directly applied to the fibre. They can, however, be produced upon the fibre itself. This method is employed to a considerable extent to produce beautiful and fast colors upon piece-goods, and in calico printing. Colors thus produced are true "ingrain colors."

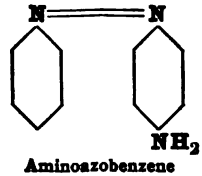
The term "ice colors," often used, refers to the necessity of keeping the bath cooled with ice, so that the diazo component of the dye shall not decompose before it is coupled with the other constituent.

The components for an azo dye to be thus developed on the fibre are, first, a phenol or amine, and second, a diazotized base. The process introduced in 1880 chiefly consists in saturating the fibre with an alkaline solution of a phenol, drying, and then passing into a cold neutral solution of the diazo component.

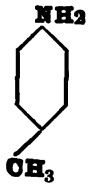
The "ingrain" or "ice colors" have become serious rivals of the alizarine dyes.

Of the various phenols available for this process, β-naphthol is used almost exclusively in practice. Of the bases, a comparatively large number are employed. These of course furnish the amino group, which is diazotized. with sodium nitrite and acid. A list of bases frequently employed is appended:

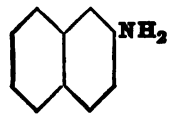
Aniline



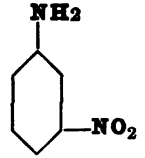
Aminoazobenzene



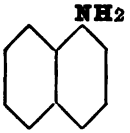
Paratoluidine



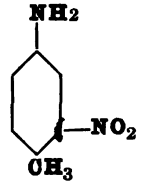
β-Naphthylamine



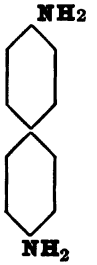
Metanitraniline



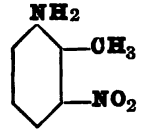
α-Naphthylamine



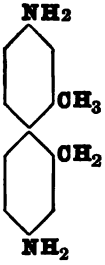
Nitroparatoluidine



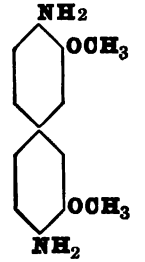
Benzidine



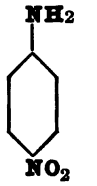
Nitroorthotoluidine



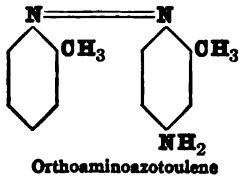
Tolidine



Dianisidine



Paranitraniline

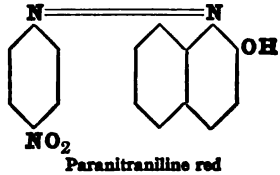


Orthoaminoazotoulene

Paranitraniline Red (1889) is an ingrain color, insoluble in water, and cannot, of course, be sold as a finished dye and ready for application. It comes into commerce in the form of its two components, paranitraniline and β-naphthol.

A mixture of paranitraniline, and the sodium nitrite necessary to diazotize it afterward, is sold as nitraniline N. The paranitraniline actually diazotized is also on the market from one firm as Azophosphor Red and as Nitrasol from another firm. The stability of the compound is maintained by a patented use of anhydrous alum as a drier.

The finished dye as it exists upon the cotton fibre has the composition indicated; the color is scarlet.

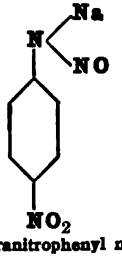


Paranitraniline red

Cotton dyed with paranitraniline red yields some of its dye to boiling alcohol and boiling benzene, which become colored orange yellow and orange respectively.

Nitrosamine Red (1893) eventually appears upon the dyed fibre identical in composition with paranitraniline red. It has, however, a different history during the development of the dye from paranitraniline. This was put upon the market by the Badische Anilin und Sodafabrik, which makes use of the property of diazo compounds to go into a stable nitrosamine condition, if treated with an alkali.

The nitrosamine red sold by this firm is a paste which consists of the sodium salt of paranitrophenyl nitrosamine:



Sodium paranitrophenyl nitrosamine

which is the result of caustic soda acting upon paranitrodiazobenzene chloride as follows:

$$\underset{\text{p-Nitrodiazobenzene chloride}}{NO_2C_6H_4—N:NCl} + 2NaOH = NO_2C_6H_4N(Na)—NO + NaCl + H_2O$$

Sodium-p-nitrophenylnitrosamine

When this product is treated with an acid it is changed back into the diazo form and exhibits the capacity of furnishing dyes by combining with phenols. If β-naphthol is employed, then the product is the same as paranitraniline red described above.

Tetrazo Dyes

In the azo dyes thus far considered the azo group, —N:N—, has occurred but once in the molecule of the dye. The number of compounds which are possible is very great, on account of the various different substances which contain the amino group, and therefore can form diazo compounds. This number is further increased because of the large number of substances which may be used as second component with the diazo derivative of each initial amine chosen.

The tetrazo dyes contain two of the azo groups, —N:N—, in a molecule. The process of double diazotization does not involve any new principle. It requires that the second component of an azo dye shall contain an amino group which may in turn be diazotized.

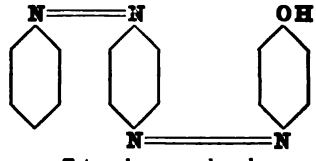
Aminoazobenzene is a type of a diazo compound which is capable at once of a second diazotizing by sodium nitrite and an acid.

$$\underset{\text{Aminoazobenzene}}{C_6H_5N:NC_6H_4NH_2}$$

By diazotizing this and combining it with phenol, for example, there results:

$C_6H_5N:NC_6H_4N:NC_6H_4OH$

Benzene azobenzene azophenol
or tetrazobenzene phenol

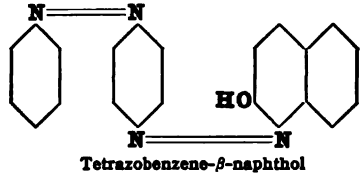


Tetrazobenzene phenol

By employing β-naphthol as the last component we have a tetrazobenzenenaphthol, whose formula is:

$C_6H_5N:NC_6H_4N:NC_{10}H_6OH$

Tetrazobenzene-β-naphthol



Tetrazobenzene-β-naphthol

TETRAZOBENZENE-β-NAPHTHOL

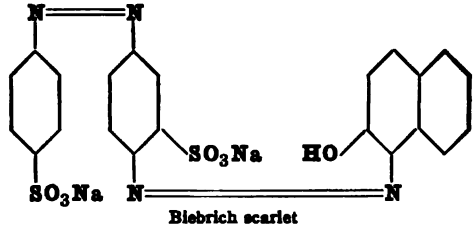
This latter substance is a most frequently occurring complex or skeleton in many dyes. As it stands, it forms a brick red powder, or brown plates with a greenish lustre. Alkalies do not dissolve it; alcohol dissolves it with difficulty; glacial acetic acid dissolves it more freely.

The sulpho groups which are necessary to the solubility of these dyes in water may occur in various positions in the molecule, sometimes in one benzene ring, sometimes in the other, or in both simultaneously, and the same is true of the naphthalene radical and the benzene rings; the sulpho group may occur in one or more, and in a great variety of positions.

The position of the sulpho group is not without influence upon the resulting compound when it is treated with concentrated sulphuric acid.

Those compounds which contain the sulpho group in the benzene nuclei are turned green by sulphuric acid; those which have one or more sulpho groups in the naphthalene nucleus are changed to violet; and, lastly, those which have sulpho groups simultaneously in both benzene and naphthalene nuclei become blue with sulphuric acid.

Biebrich Scarlet (1878), Ponceau B. Extra, Ponceau 3R.B., New Red L., Imperial Scarlet is a brownish red powder which forms an orange red solution in water. In its preparation aminoazobenzene disulphonic acid is diazotized and then combined with β-naphthol; the sodium salt of the product is shown structurally:



Biebrich scarlet

This yields with concentrated sulphuric acid a green color, which addition of water turns first to blue and then causes the brownish red flocks to separate. From a concentrated solution of the dye, hydrochloric acid precipitates red flocks, and a brownish red precipitate is caused by caustic soda: this dissolves with a violet color in pure water.

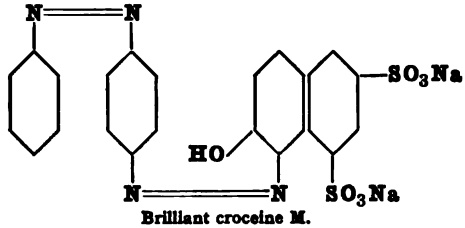
Wool and silk are dyed from an acid bath a bluish shade of scarlet. The color resists acids and alkalies; it is fast to milling, moderately fast to light, but sensitive to sulphur.

By comparison with the following dye, brilliant croceine M., the effect may be observed of shifting both sulpho groups from the benzene rings to the naphthalene nucleus.

Brilliant Croceine M. (1882), Cotton Scarlet 3B., Brilliant Crociene has the same composition as the Biebrich scarlet described above and is an isomer whose difference depends upon the changed position of the two sulpho groups.

It is manufactured from aminoazobenzene which is diazotized and coupled with β-naphthol disulpho acid γ.

The commercial dye is the sodium salt of the resulting compound, whose structure is:



Brilliant croceine M.

The two sulpho groups, no longer distributed one to each benzene nucleus, are both fixed in the naphthalene nucleus and their change of position imposes a change in shade upon the dyestuff, when used upon wool or silk from a bluish scarlet to scarlet.

The dyestuff is a light brown powder which gives a cherry red aqueous solution. A brown precipitate falls from its solution on adding hydrochloric acid. Caustic soda changes the color to brown instead of producing a brownish red precipitate, as in the case of its isomer Biebrich scarlet. It dissolves in strong sulphuric acid with a reddish violet color, which changes to blue and then deposits a brown precipitate as water is gradually added.

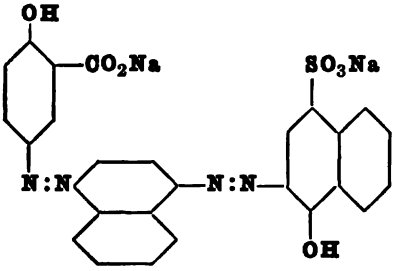
Wool and silk are dyed red from an acid bath. Paper and cotton with an alum mordant may also be dyed red. The color is fast to light and acids but not to washing. Lakes may be produced with aluminum hydrate and with barium chloride.

Diamond Black F. (1889) is a tetrazo dye chosen for comparison with the next dye described, in order to show the change in the color caused by a second hydroxyl introduced into this dye.

The manufacture of diamond black F. requires the following substances to be diazotized and coupled in the order represented in the diagram:

Aminosalicylic acid azo α-naphthylamine + α-naphthol sulpho acid N. W.

The sodium salt of the dye, which occurs in commerce as a brownish black powder, has the following structure:



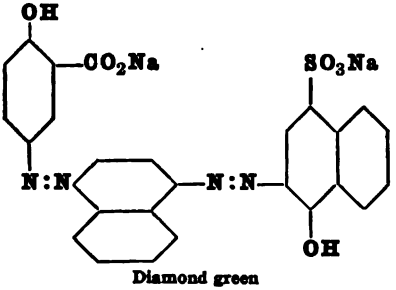
Diamond black F.

A violet precipitate falls from the aqueous solution of this dye on adding hydrochloric acid. The color merely changes to blue, if caustic soda is added.

Wool mordanted with chromium salts is dyed a bluish black.

Diamond Green (1890) is an acid azo dye which is used to dye chromium-mordanted wool a dark bluish green. It differs in composition from diamond black F., just described, by the addition of one oxygen atom, which forms an additional hydroxyl group in position 8 of the second naphthalene nucleus, as shown in the structural formula below.

The manufacture of the dye requires the three substances aminosalicylic acid, α-naphthylamine, and 1.8-dioxynaphthalene-4-sulpho acid to be diazotized and coupled in the order named. The sodium salt of the product is the commercial dye of the following constitution:



Diamond green

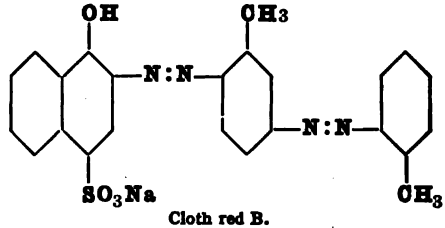
As one extra hydroxyl group is the only feature in which this dark green dye differs from the previous black one, the change in color attends this change in composition.

It is a black powder which gives a dark violet colored aqueous solution. Hydrochloric acid produces a dark violet precipitate, while caustic soda turns the solution to a dark blue color. The solution in strong sulphuric acid is bluish green: water changes it to greenish blue and if added in large amounts a dark violet precipitate falls.

The bluish green color dyed upon chromium-mordanted wool is fast to light, to acids and alkalies, and also to milling.

Cloth Red B. (1879) is a tetrazo dye which is employed to replace the older santal wood. Upon wool mordanted with chromium salts, it dyes red.

In its preparation, aminoazotoluol, $C_6H_4N:NC_6H_3(CH_3)NH_2$, is diazotized and then combined with a naphthol disulpho acid Sch. The structural formula of the sodium salt which is the commercial dye exhibits the constitution of the components and the finished dyestuff.



Cloth red B.

The dyestuff appears as a dark brownish red powder which is soluble in water with a red color. Hydrochloric acid causes a red precipitate while a violet coloration follows the addition of caustic soda.

Black Dyes

The first black tetrazo dye was discovered in 1883. In all these dyes there is to be observed a central naphthalene nucleus which seems to impose upon the dyes containing it some one of the darker colors. As a basis of the black dyes

there may be noticed one of the three following complexes or compound nuclei:

$$C_{10}H_7N:NC_{10}H_6N:NC_{10}H_7,$$

or

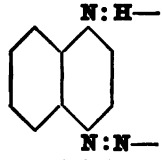
$$C_6H_5N:NC_{10}H_6N:NC_{10}H_7,$$

or

$$C_6H_5N:NC_{10}H_6N:NC_6H_5.$$

In the order of their diazotizing, the three substances in each complex form the components, and in each complex the same nucleus appears, because α-naphthylamine is in each case employed as the second component.

Thus in each appears this group:

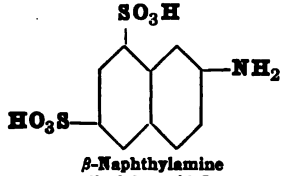


Central group of black tetrazo dyes

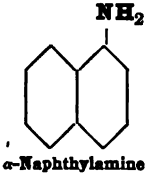
Aniline and naphthylamine sulpho acids form most frequently the first components, and the different naphthol sulpho acids serve as third components.

The process of manufacture for all consists in diazotizing the first component, combining this diazo product with the second component to form an amino azo compound, diazotizing again and coupling the third component.

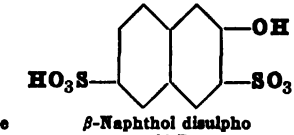
Naphthol Black B. (1885), Brilliant Black B. was the first of these black dyes to win technical importance. The initial component is β-naphthylamine disulpho acid G. of the following constitution; the other two components are placed alongside for comparison:



β-Naphthylamine disulpho acid G. First component



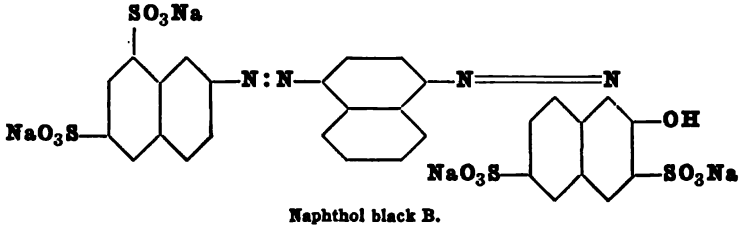
α-Naphthylamine Second component



β-Naphthol disulpho acid R. Third component

When the diazo compound of the first component unites with the second, it joins itself to position 4 of that substance, thus leaving in position 1 the amino group, which renders it capable of the second diazotization requisite to enable it in turn to couple with the third component, wherein position 1 is the point of attachment.

The sodium salt of the finished dyestuff has the following constitution:



Naphthol black B.

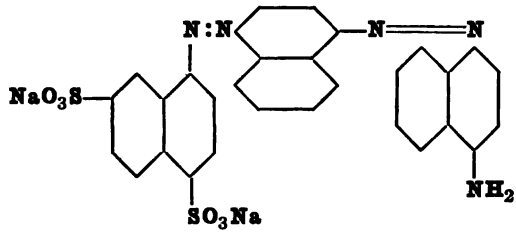
Naphthol Black B. is a bluish black powder which yields a violet colored aqueous solution. A reddish violet precipitate falls on adding hydrochloric acid to its aqueous solution. Caustic soda causes a blue precipitate which in pure water redissolves. Concentrated sulphuric acid forms with it a green solution which on diluting turns blue and then lets fall a red violet precipitate.

In an acid bath wool is dyed a bluish black. The dyed color is fast to light and resists the action of alkalies and acids.

Naphthylamine Black D. (1888) is a tetrazo dye whose dyeings are less affected by milling than naphthol black, but its resistance to acids is not so great.

It is prepared from α-naphthylamine disulpho acid 1:4:7, which after diazotizing is coupled with α-naphthylamine, and then after a diazotization of this product coupled again with a second molecule α-naphthylamine.

The sodium salt of the dye is shown so that the various components may be identified:



Naphthylamine black D.

The dyestuff is a black powder which in water gives a violet black solution. Addition of hydrochloric acid causes a black precipitate and caustic soda produces a precipitate of the same color, which is soluble in pure water. It forms a bluish black solution in strong sulphuric acid which turns green as water is added and then a black precipitate separates.

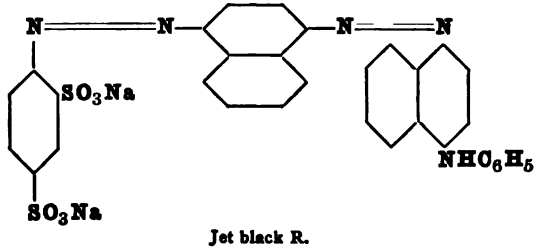
Wool and silk are dyed black from an acid bath or from a neutral bath by the aid of salt. It is moderately fast and it is suitable for dyeing mixed wool and cotton goods.

Naphthylamine Black 4B. is a dyestuff prized for the beautiful logwood shade of its dyeings. It is not a single pure dye, but a mixture of naphthylamine black D. and naphthol blue black, which will be described later.

Jet Black R. (1888) is a tetrazo dye suitable for a beautiful blue black on wool and also adapted for dyeing silk a dark blue or black, according to the amount of dyestuff employed.

The dye is prepared from aniline 2-4-disulpho acid, which is diazotized and combined with α-naphthylamine, diazotized again, and coupled with phenyl α-naphthylamine.

The sodium salt is:



Jet black R.

It is a black powder whose aqueous solution is colored violet. A bluish black precipitate falls on the addition of hydrochloric acid. A soluble violet precipitate falls on the addition of caustic soda.

The dye imparts a bluish black color to wool from a bath containing acetic acid or from a neutral bath with the addition of common salt. Silk is dyed from a bath acidulated with acetic acid or from a boiled-off bath containing acetic acid.

The color is not sensitive to acids and alkalies and it is moderately fast to light and milling.

Substantive Cotton Dyes

Cotton is the cheapest and most abundant fibre which is employed on an enormous scale for spinning and weaving. Yet, while it is so much less costly than silk or wool, it has been the most difficult and expensive fibre to dye in a satisfactory manner. The slight affinity of the cotton fibre for the various dyes does not allow of a fixation of color which will resist washing.

To enable cotton to become permanently dyed, the fibre had first to be impregnated with an acid or basic mordant, which was capable of a double affinity one for the fibre and one for the subsequently applied dye. This extra manipulation and the limiting of the kinds of dyes that could be employed greatly increased the relative and absolute cost of successfully coloring cotton fabrics.

But three of the natural dyestuffs were exceptional in their ability to color cotton without a mordant, and these were curcuma, safflower, and Orleans.

In the year 1884 the history of cotton dyeing shows an epoch-making change. A discovery in the field of the azo dyes by Böttiger was responsible for this. He discovered Congo red, a dye capable of imparting an intense red to cotton which had not been previously prepared by mordants. Congo red was the first of a long series of dyes which could dispense with fixing agents upon cotton.

These new dyes were derived from benzidine, $H_2NC_6H_4—C_6H_4NH_2$, but this substance soon found rival substances which could replace benzidine in the manufacture of similar dyes, and because of this the term "substantive cotton dyes" was applied to them.

As some of these colors are even more suitable for wool than for cotton, the term was inappropriate; then, because in the application of these dyes neutral or alkaline salts were employed in the dye-vats, they were more appropriately called "salt dyestuffs."

Considering the vast amount of cotton manufactured in comparison with wool and silk and that these dyes so simplify the methods of application, it can be easily understood that the greatest rewards of the dye industry are attained in this field.

Benzidine

Benzidine, which is the starting point of a large number of these dyes, is prepared from nitrobenzene by reducing it in alkaline solution; the nascent hydrogen being evolved from zinc dust and caustic soda and the mass contained in an iron vessel being rapidly agitated.

A steam distillation removes the aniline that is formed, and subsequent treatment with cold dilute hydrochloric acid removes the zinc hydrate. The hydrazo benzene which is left insoluble from the above treatment is converted into the isomeric benzidine by boiling with hydrochloric acid, when the following molecular rearrangement takes place.

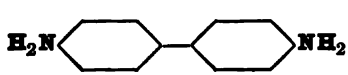
$$\underset{\text{Hydrazo benzene}}{C_6H_5NH—NHC_6H_5} + HCl = \underset{\text{Benzidine}}{H_2NC_6H_4—C_6H_4NH_2} + HCl$$

The solution after filtration is treated with sulphuric acid or sodium sulphate, which precipitates the benzidine as insoluble sulphate. The free base benzidine is obtained by decomposing the sulphate with caustic soda and distilling.

Congo red employs the diamino compound: benzidine, which allows a double diazotization, and a subsequent coupling

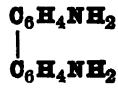
of two molecules of naphthionic acid to the tetrazo diphenyl chloride produced from the benzidine.

The constitutional formula of benzidine is as follows:



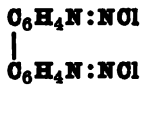
Benzidine

or

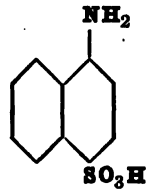


Benzidine

Congo red requires the diazotizing of both the amino groups of benzidine with the production of tetrazodiphenyl chloride.



Diazotized benzidine or tetrazo diphenyl chloride



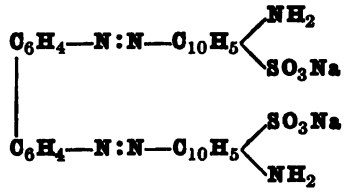
Naphthionic acid

The two molecules of the second component, naphthionic acid, do not unite with the tetrazo compound with equal rapidity. While the union of one molecule is carried out quickly, the second molecule requires a considerable time to elapse before the operation is completed.

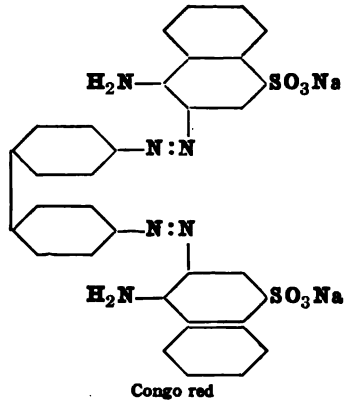
With Congo red, this second operation lasts from one to two days: with benzopurpurine, five to six days are required for completion.

The operation may be hastened by employing a large excess of the second component.

The commercial dyestuff is the sodium salt of the following complex body:



or,



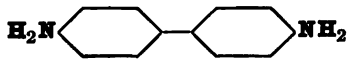
Congo red

The dyestuff is a reddish brown powder which imparts the same color to its aqueous solution. The addition of hydrochloric acid produces a blue precipitate: even dilute acetic acid throws down a bluish violet precipitate. A reddish brown soluble precipitate falls on adding caustic soda.

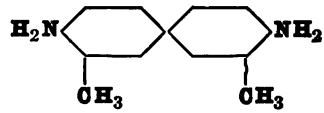
Cotton and wool are dyed red directly from an alkaline salt bath. It is not fast to light, and it has the additional disadvantage of great sensitiveness to acids, traces of which turn it instantly blue. Indeed, its great sensitiveness to acids has caused it to be used as an indicator in volumetric analysis.

In spite of its defects through lack of fastness to light and its extreme sensitiveness to acid, it is dyed upon large amounts of material sent to Eastern Asia.

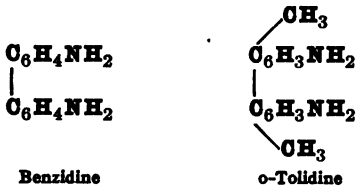
Benzopurpurin 4B. (1885), Cotton Red 4B. is a direct cotton dyestuff which stands in close relation to the Congo red just described, for it is the second higher homologue of that color. In the benzidine nucleus are fixed two methyl groups in the ortho position to the amino groups of the benzine rings, as shown below. This dimethyl derivative of benzidine is known as *o*-toldidine.



Benzidine

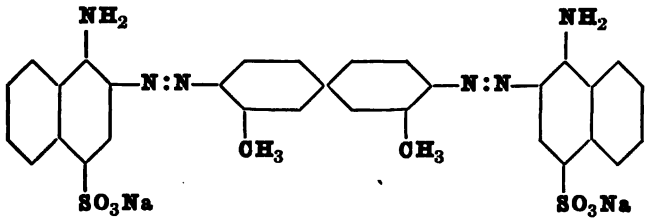


o-Tolidine



Benzidine o-Tolidine

The *o*-tolidine is diazotized and the second components are the same are for Congo red, viz., naphthionic acid or 1-amino-naphthalene-4-sulpho acid and they are coupled to produce the dyestuff. The sodium salt is shown below:



Benzopurpurin 4B.

The influence of these two methyl groups is to produce in dyeing a yellower and more lively shade of red and to render the color less delicately sensitive to acids.

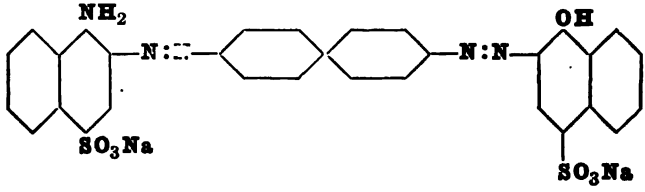
It forms a brown powder which communicates a brownish red color to its aqueous solution. A blue precipitate falls on adding hydrochloric acid. Dilute acetic acid causes a brown precipitate, while no change is made by caustic soda. The blue solution in concentrated sulphuric acid yields a blue precipitate when water is added.

Cotton is dyed red from a soap bath.

Congo Corinth G. (1886) is a tetrazo dye, and a near relative of Congo red. It dyes cotton a brownish violet and this change of color from the Congo dye may be attributed to the replacement of an amino group by a hydroxyl group.

The initial substance is benzidine: this, after being diazotized, is coupled with one molecule of naphthionic acid and one molecule of 1-naphthol-4-sulpho acid. Thus, the hydroxyl is carried into the dye molecule by the latter substance.

The sodium salt of the dye is shown in the structural formula, which allows an easy comparison with Congo red:



Congo Corinth G.

The hydroxyl group in replacing an amino group impels a change of color from red to brownish violet.

The dyestuff forms a greenish black powder which gives a rosaniline color to its aqueous solution. Hydrochloric acid causes a violet precipitate, while caustic soda turns the solution cherry red, and then causes a red soluble precipitate to fall.

Cotton is dyed a brownish violet from a weakly alkaline soap bath. The color is not fast to light, though moderately fast to washing. Alkalies redden the color and it exhibits a sensitiveness to acids.

Acid and Alkaline Solutions for Tetrazo Dyes

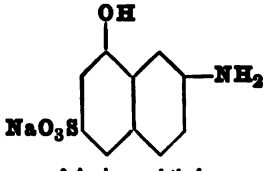
When the initial substance employed in the manufacture of an azo dye has been converted by sodium nitrite and an acid into a diazo compound, it is ready for coupling the second components. In this operation of coupling a choice is offered of either an acid or an alkaline solution. The results will be different in the two cases: different substances with different colors will be formed even though the constituent substances used are the same.

The two following dyes, diamine violet N. and diamine violet R.O., exhibit the results above described.

Diamine Violet N. (1889) is a benzidine dyestuff which colors cotton violet without a mordant from a weakly alkaline bath or from a neutral bath containing sodium sulphate.

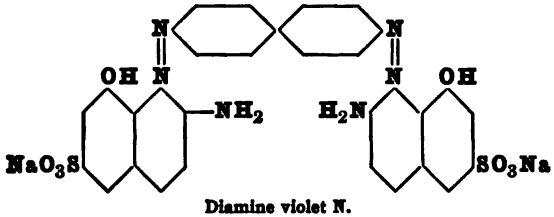
The diazotized benzidine is coupled in an acid solution

with two molecules of β-aminonaphtholsulpho acid, γ, whose composition is:



β-Aminonaphthol-sulpho acid γ.

The sodium salt of the finished dyestuff has the following constitution:



Diamine violet N.
Finished in acid solution

The commercial dye is a dark brown powder which is soluble in water with a reddish violet color. Hydrochloric acid causes a violet precipitate inclining to black. The solution is unchanged by caustic soda.

The violet color imparted to unmordanted cotton is fast to light, acids and washing.

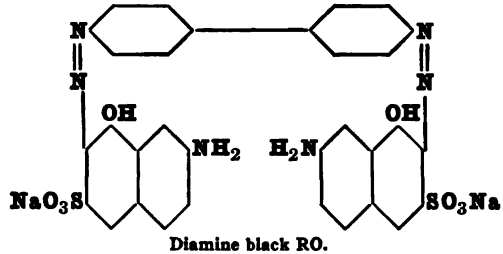
Wool or silk in a neutral or weakly alkaline bath are colored a violet which is not fugitive to light and is fast to washing and milling and resists the action of acids and alkalies.

The dye is also employed upon mixed wool and silk fabrics.

Diamine Black R. O. is made from the same constituents as diamine violet N. described above, but the final operation is here carried out in an alkaline solution where that dyestuff required an acid one.

Diazotized benzidine is coupled with β-aminonaphtholsulpho acid, γ, in an acid solution. This difference in condition causes the diazo compound to attach itself to the

second components at different points, as the completed molecule of the dye will show.



Diamine black RO.
Finished in alkaline solution

By comparing this formula with that of diamine violet N., it will be noticed that the alkaline solution has caused the diazo benzidine to attach itself to two beta positions instead of two alpha positions, or to position 7 in place of position 1, as in the former dye.

Thus, though this dye is an isomer of the former, it dyes grayish violet upon unmordanted cotton, or when diazotized upon the fibre itself, and then combined with β-naphthol and resorcin develops a black.

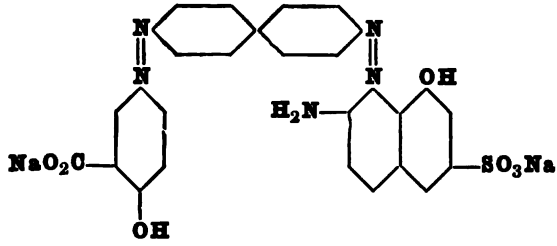
The commercial dye is a black powder which colors its aqueous solution a violet black. A blue precipitate is caused by hydrochloric acid. A violet coloration results on adding caustic soda.

The colors upon cotton are fast to light and washing and they resist the action of acids and alkalies.

Diamine Fast Red F. (1889) is a benzidine dye which exhibits the result of changing one of the second components with which diazotized benzidine is coupled in acid solution.

When the benzidine is diazotized and ready for coupling, it is allowed to satisfy one diazo group with β-aminonaphthol-sulpho acid, γ, and the other diazo group is coupled with salicylic acid.

The structure of the finished dye exhibits the difference in the second components, which changes a diamine violet into a red dye.



Diamine fast red F. Finished in acid solution

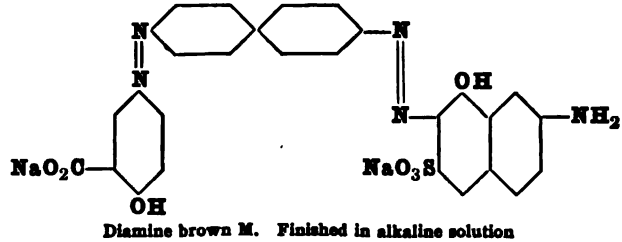
The dye is a brownish red powder soluble in water with a red color. Hydrochloric acid throws down a red precipitate, caustic soda produces a soluble red precipitate. A reddish blue solution in strong sulphuric acid gives a brown precipitate as water is added.

Cotton is dyed red in a boiling bath containing a large amount of sodium sulphate and strongly alkaline with caustic soda. Chromium-mordanted wool is also dyed red. It also imparts a very fast color to silk in an acetic acid bath.

Diamine Brown M. (1889) is an illustration among the benzidine dyes of the effect of an alkaline solution in place of an acid one when the diazotized benzidine is joined to the same components that were used in producing diamine fast red F. above.

The effect of coupling the diazotized benzidine in alkaline solution is to change the place where it shall attach itself in the molecule of β-aminonaphtholsulpho acid. In this instance it becomes attached in a beta position, while in the acid solution it chooses an alpha position. The other component salicylic acid does not change its behavior.

The completed molecule shows this brown dye to be an isomer of the above red one, and the following formula shows the difference in structure.



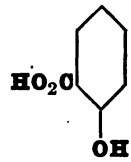
Diamine brown M. Finished in alkaline solution

It appears in commerce as a brown powder which is soluble in water with a reddish brown color. Hydrochloric acid throws down a brown precipitate and caustic soda causes a soluble reddish brown precipitate to fall. It forms a violet solution in strong sulphuric acid, and on diluting it with water the color changes to brown and a brown precipitate falls.

Cotton is dyed brown in an alkaline bath to which sodium sulphate has been added. After-treatment with copper sulphate renders the dye faster to light. The color is moderately fast to light and washing, and it is likewise fast to acids and alkalies.

Chrysamine G. is a dyestuff so sensitive to the action of copper that its solutions should not be allowed to come in contact with vessels of that metal, otherwise the color will be dulled.

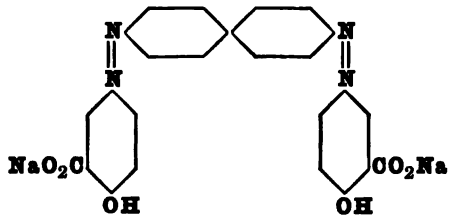
It is a benzidine dye. When benzidine is diazotized it is joined to two molecules of salicylic acid.



Salicylic acid

The change from the two molecules of naphthionic acid which are joined to diazotized benzidine in Congo red to the two molecules of salicylic acid is responsible for the lightening of the color from red to yellow.

The sodium salt is the commercial dye and its structure is:



Chrysamine G.

It forms a yellowish brown powder or a yellow paste which is very difficultly soluble in water to a brownish yellow color.

A brownish precipitate falls on the addition of hydrochloric acid. Caustic soda turns the solution orange red and then causes an orange red soluble precipitate. If the reddish violet solution in strong sulphuric acid be diluted, a brown precipitate falls.

Cotton is dyed yellow from a soap bath.

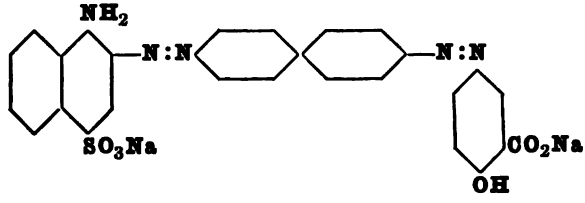
It forms chromium lakes and it is used for producing cream colors in cotton printing. The color is fast to light and moderately fast to washing.

Benzo Orange R. (1887), Direct Brilliant Orange 3R. is a benzidine dyestuff wherein the diazotized benzidine is coupled with different secondary components.

It has been shown that in the Congo red two molecules of naphthionic acid formed the second components, and in chrysamine G. two molecules of salicylic acid combined with diazotized benzidine to form a yellow dye.

In the present instance benzo orange R. results as a mean between the red and yellow dyes and, in fact, it contains, joined to benzidine, one molecule of salicylic acid used in chrysamine yellow and one molecule of naphthionic acid used in Congo red.

The sodium salt of benzo orange has the following composition, and its formula betrays a likeness both to Congo red and chrysamine G.



Benzo orange R.

The dyestuff appears as a brownish red crystalline body which is soluble in water with a reddish yellow color. It

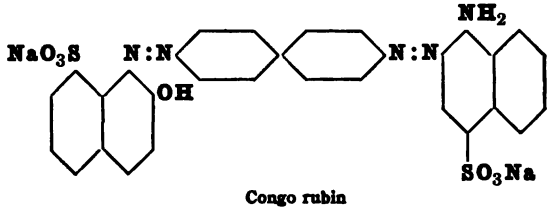
turns reddish violet with the addition of hydrochloric acid.

In a concentrated solution, a reddish yellow precipitate falls on adding caustic soda. A violet blue solution is formed with strong sulphuric acid and a grayish violet precipitate falls when sufficient water is added.

Cotton and chromium-mordanted wool are dyed an orange color which is fast to light but sensitive to acids.

Congo Rubin (1891) is prepared from diazotized benzidine and one molecule of 2-naphthol-8-sulpho acid, known as β-naphtholmonosulpho acid B., and also one molecule of 1-aminonaphthalene-4-sulpho acid, known as naphthionic acid.

In comparison with the two following dyes it illustrates the change of color induced by changing one of the secondary components. The constitutional formula of the sodium salt of the dyestuff is:

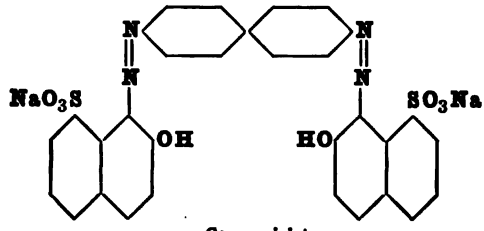


Congo rubin

The dye forms a greenish crystalline powder which gives a cherry red aqueous solution. A pure blue precipitate is produced by hydrochloric acid and a violet red precipitate by caustic soda.

Cotton is dyed directly a rosaniline red color.

Congo Violet (1883), **Bordeaux** (**extra**) is formed like the dye Congo rubin, described above, in so far as diazobenzidine and one of the secondary components 2-naphthol-8-sulpho acid, but the other secondary is in this dyestuff also 2-naphthol-8-sulpho acid. The two secondary components are here both alike and the dye is a violet in place of red. The comparison of the following formula with that of Congo rubin will show the difference in structure:

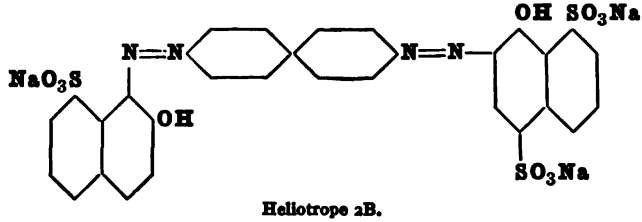


Congo violet

Congo violet appears in commerce as a brown powder which gives a red aqueous solution. Addition of hydrochloric acid to this solution throws down a violet precipitate. Caustic soda only turns it yellower.

Cotton from a salt bath is dyed violet, while wool is dyed red from an acid bath.

Heliotrope 2B. (1892) is a benzidine derivative which is manufactured by coupling diazotized benzidine with 2-naphthol-8-sulpho acid for one component and then with 1-naphthol-4-8-disulpho acid. The first of these components is the same as that for both Congo rubin and Congo violet, but the change in the second component develops the heliotrope violet color of the dye. From the following formula, it will be seen that on comparison with Congo violet one hydroxyl group has changed position with the point of fixation of the diazo benzidine: a second sulpho acid group has also entered at position 4.



Heliotrope 2B.

The dyestuff is a dark gray powder whose aqueous solution is reddish violet. A bluish violet precipitate is caused by hydrochloric acid, while caustic soda causes only a reddening of the solution.

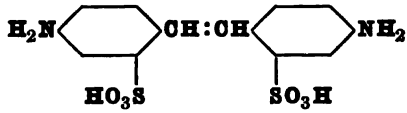
Cotton is dyed heliotrope without the aid of a mordant.

Diamino Stilbene Disulpho Acid

A large number of amines beside benzidine, which has been spoken of most frequently in the preceding pages, are used as starting points for the manufacture of the tetrazo dyes.

The prime requisite is the presence of two amino groups which offer themselves to a double diazotization, and many substances possessing among their various side groups the two amino groups are readily available for initial substances of the more complex tetrazo dyes.

Diamino stilbene disulphonic acid is an example of such a class of substances. The composition is shown below:

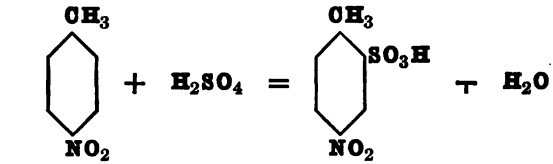


Diamino stilbene disulpho acid

It resembles in its configuration benzidine; indeed if a molecule of benzidine is imagined to be cut in half and the two carbon and hydrogen atoms thrust between the benzene rings, a molecule of stilbene would be formed.

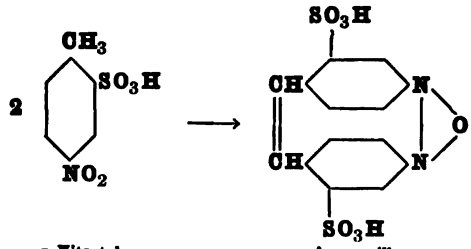
In preparing this substance *p*-nitrotoluene is treated with fuming sulphuric acid and a sulpho group is introduced, forming *p*-nitrotoluene sulpho acid. This product on boiling with caustic potash yields azoxystilbene disulpho acid. Zinc dust is then added to the alkaline solution setting free nascent hydrogen, which reduces it and decolorizes it, forming diamono stilbene disulpho acid.

The transformations which take place are indicated below so as to show the relative positions of the substituting groups in the partial and final products:



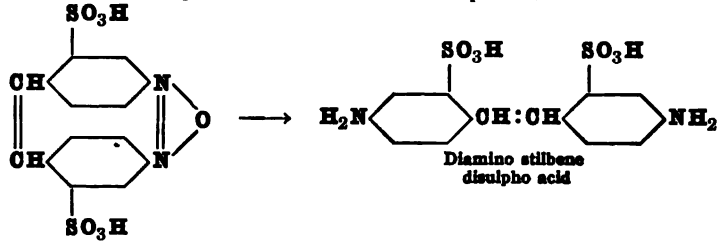
p-Nitrotoluene

p-Nitrotoluene sulphonic acid



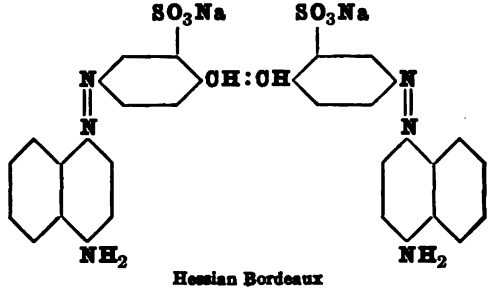
p-Nitrotoluene sulphonic acid

Azoxystilbene disulpho acid



Diamino stilbene disulpho acid

Hessian Bordeaux (1886) is a tetrazo dye which requires diamino stilbene disulpho acid as its starting point. This substance after diazotizing is coupled with two molecules of α-naphthylamine. This dye, in comparison with the Hessian purple N, shows the effect of a change in position of the amino groups upon the color of the dye. The composition and structure of the sodium salt of the completed dyestuff is shown below:



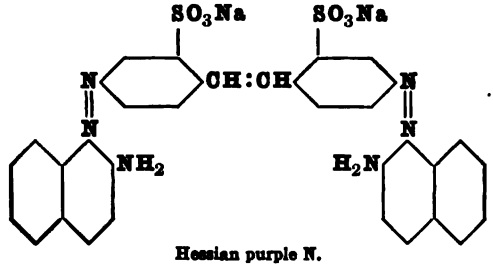
Hessian Bordeaux

The commercial dyestuff is a greenish shining powder which imparts a deep red color to its aqueous solution.

A blue precipitate falls on addition of hydrochloric acid, while caustic soda causes a red precipitate.

Unmordanted cotton is colored Bordeaux red. It may be diazotized upon the fibre itself.

Hessian Purple N. (1886) resembles the last dye Hessian Bordeaux described, indeed it is an isomer of it. The same compound diamino stilbene disulpho acid is used as the starting point. When it has been diazotized, it is coupled with two molecules of β-naphthylamine. The result is a molecule of the dye in which the amino groups are in the neighboring carbon atoms to those which are joined to the two azo groups. The formula of the sodium salt, which is the dye, is the following:



Hessian purple N.

By referring to the formula of Hessian Bordeaux, the amino groups will be found attached to those carbon atoms which are opposite to those which engage the diazo groups. This change in position changes the color of the dye from Bordeaux red to purple.

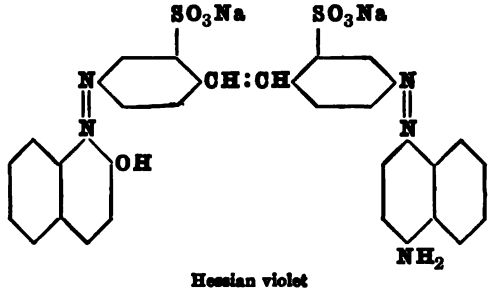
Hessian Purple N. is a brownish red powder. Its aqueous solution is cherry red. A bluish black precipitate falls on adding hydrochloric acid. Caustic soda gives a red precipitate which readily dissolves in a large amount of water.

Cotton is dyed a bluish red from a soap bath. The color is not fast to light and it is sensitive to acids. It is less fugitive upon wool than upon cotton, and it is moderately fast to milling.

Hessian Violet (1886) may be regarded a relative of Hessian Bordeaux, for if one amino group be removed and a hydroxyl group be substituted in the same naphthalene nucleus, though in a different position, a red dye becomes violet.

Diazotized diamino stilbene disulpho acid is united with one molecule of α-naphthylamine and one molecule of β-naphthol

with the result shown below in the formula of the sodium salt of the dyestuff, which is the commercial product:



Hessian violet

The commercial dye is a black powder. It dissolves in water with a reddish violet color. Hydrochloric acid throws down a blue precipitate. A bluish violet color results on adding caustic soda.

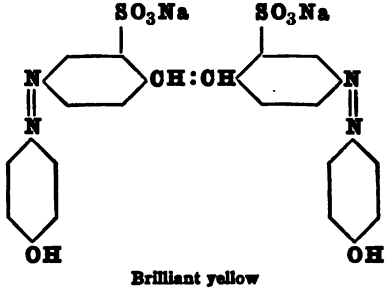
Cotton is dyed violet without a mordant from a soap bath. The color is fugitive to light and rather sensitive to acids.

Brilliant Yellow (1886) appears as an orange red powder which gives a reddish yellow solution in water.

It is a tetrazo dye which requires the same initial substance as the three preceding dyes, but the secondary components of less molecular weight.

Diazotized diamino stilbene disulpho acid is joined to two molecules of carbolic acid or phenol. The point of attachment of the azo groups is that opposite to the hydroxyl of the phenol in each instance.

The structure is shown as follows:



Brilliant yellow

A violet precipitate is thrown down from its aqueous solution upon adding hydrochloric acid. A yellowish red coloration results when caustic soda is added.

Cotton is dyed yellow from an acid bath. It is very fast to light, though sensitive to alkalis. Dilute acids do not affect it.

The color is reddened by alkalis. It is used more for coloring paper than cotton.

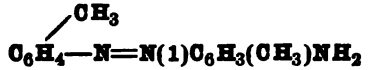
Representative Azo Dyes

The following tables contain representative azo dyes which are classified according to the number of azo groups present in them and according to the methods of formation which are explained in the preceding pages.

Name. Components Coupled by Diazotizing.

Spirit Yellow R.

o-Toluidine + *o*-Toluidine

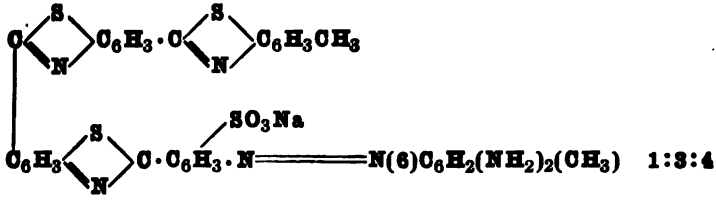


$C_6H_4(CH_3)—N=N(1)C_6H_3(CH_3)NH_2$ 3:4

Colors fats, oils, waxes and lacquers.

Atlas Red.

Primuline + *m*-Toluylene Diamine

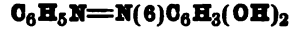


$C_6H_3(SO_3Na)$ C_6H_3 $N=N(6)C_6H_2(NH_2)_2(CH_3)$ 1:3:4

Dyes unmordanted cotton in an alkaline bath terra cotta red.

Sudan G.

Aniline + Resorcin



$C_6H_5N=N(6)C_6H_3(OH)_2$ 1:3

Used in coloring fats and oils.

NAME. COMPONENTS COUPLED BY DIAZOTIZING

Sudan I.

Aniline + β-Naphthol

$C_6H_5N{=}N(1)C_{10}H_6OH$ 2

Colors spirit varnishes and oils orange yellow.

Orange G.

Aniline + β-Naphthol γ-Disulpho Acid

$C_6H_5N{=}N(1)C_{10}H_4(OH)(SO_3Na)_2$ 2:6:8

Employed in wool dyeing for mixed shades.

Alizarine Yellow G.G.

m-Nitraniline + Salicylic Acid

$(NO_2)C_6H_4N{=}N(1)C_6H_3(CO_2H)(OH)$ 3:4

Dyes wool mordanted with chromium salts yellow.

Alizarine Yellow R.

p-Nitraniline + Salicylic Acid

$(NO_2)C_6H_4N{=}N(1)C_6H_3(CO_2H)(OH)$ 3:4

Dyes wool mordanted with chromium salts yellowish brown.

Victoria Violet 4B.S.

Reduction product of Chromotrope 2B. in Alkaline Solution

$H_2NC_6H_4N{=}N(2)C_{10}H_3(OH)_2$ 1:8 $(SO_3Na)_2$ 3:6

Wool is dyed a bluish violet in an acid bath. The dye equalizes well and is fast to washing and rubbing.

Cochineal Scarlet 2R.

Toluidine + α-Naphthol Sulpho Acid C.

$CH_3C_6H_4N{=}N(2)C_{10}H_5(OH)SO_3Na$ 1:5

Dyes wool in an acid bath red.

Orange G.T.

Toluidine + β-Naphthol Sulpho Acid S.

$CH_3C_6H_4N{=}N(1)C_{10}H_5(OH)(SO_3Na)$ 2:6

Wool is dyed orange yellow from an acid bath.

NAME. COMPONENTS COUPLED BY DIAZOTIZING

Azofuchsine B.

Toluidine + Dioxynaphthalene Sulpho Acid S.

$$CH_3C_6H_4N{=}N(2)C_{10}H_4(OH)_2SO_3Na \quad 1:8:4$$

Wool is dyed a rosaniline red from an acid bath.

Sudan II.

Xylidine + β-Naphthol

$$(CH_3)_2C_6H_3N{=}N(1)C_{10}H_8OH \quad 2$$

Employed for coloring fats, oils and spirit varnishes a yellowish red.

Azococcine 2R.

Xylidine + α-Naphthol Sulpho Acid N.W.

$$(CH_3)_2C_6H_3N{=}N(2)C_{10}H_5(OH)(SO_3Na) \quad 1:4$$

Wool is dyed red in an acid bath. Used largely for dyeing silk. Fast to light and not sensitive to acids and alkalis. It is sensitive to action of metals.

Wool Scarlet R.

Xylidine + α-Naphthol Disulpho Acid Sch.

$$(CH_3)_2C_6H_3N{=}N(2)C_{10}H_4(OH)(SO_3Na)_2 \quad 1:4:8$$

Wool is dyed a fiery red which resists milling and the action of light.

Brilliant Orange R.

Xylidine + β-Naphthol Sulpho Acid S.

$$(CH_3)_2C_6H_3N{=}N(1)C_{10}H_5(OH)(SO_3Na) \quad 2:6$$

Dyes wool yellowish red from an acid bath. It is also used for dyeing silk.

Ponceau 2R.

Xylidine + β-Naphthol Disulpho Acid R.

$$(CH_2)_2C_6H_3N{=}N(1)C_{10}H_4(OH)(SO_3Na)_2 \quad 2:3:6$$

Wool is dyed red from an acid bath and it is used for coloring lacquers.

NAME. COMPONENTS COUPLED BY DIAZITIZING

Ponceau 3R.

ψ-Cumidine + β-Naphthol Disulpho Acid R.

$(CH_3)_3C_6H_2N{=}N(1)C_{10}H_4(OH)(SO_3Na)_2$ 2:3:6

Dyes wool red from an acid bath and is used to color lacquers.

Sudan Brown.

α-Naphthylamine + α-Naphthol

$C_{10}H_7N{=}N(4)C_{10}H_6(OH)$ 1

Employed to color fats, oils and spirit varnishes.

Fast Red B.T.

α-Naphthylamine + β-Naphthol Sulpho Acid S.

$C_{10}H_7N{=}N(1)C_{10}H_5(OH)(SO_3Na)$ 2:6

Wool is dyed in an acid bath.

Azocochineal.

o-Anisidine + α-Naphthol Disulpho Acid Sch.

$CH_3OC_6H_4N{=}N(2)C_{10}H_4OH(SO_3Na)_2$ 1:4:8

Wool is dyed red in an acid bath which is fast to light, acids and alkalis, but less resistant to milling.

Diamond Flavine G.

Tetrazobenzidine + Salicylic Acid

(and boiling which replaces the second diazo group by OH)

$$\begin{matrix} N{-}C_6H_4C_6H_4OH \\ \| \\ N{-}C_6H_3(CO_2H),(OH) \end{matrix}$$ 3:4

Wool mordanted with chromium salts is dyed yellow.

Erika B.

Dehydrothio-m-Xylidine + α-Naphthol-e-Disulpho Acid

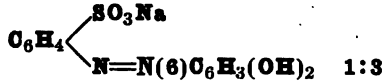
$$(CH_3)_2C_6H_2{<}\begin{matrix} S \\ \diagup\diagdown \\ -N{=}C \end{matrix}\cdot C_6H_3(CH_3)N{=}N(2)C_{10}H_4(OH)(SO_3Na)_2$$ 1:3:8

Cotton is dyed rose red without a mordant.

NAME. COMPONENTS COUPLED BY DIAZOTIZING.

Chrysoine.

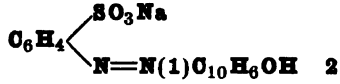
Sulphanilic Acid + Resorcine



Employed for mixed shades upon wool and silk.

Orange II.

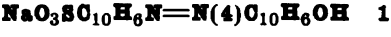
Sulphanilic Acid + β-Naphthol



Wool and silk in an acid bath are dyed orange.

Naphthylamine Brown.

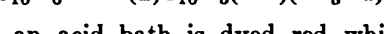
Naphthionic Acid + α-Naphthol



Dyes wool in an acid bath a brownish orange which becomes fast to washing, alkalis and acids by oxidation upon the fibre with chromic acid.

Azorubin.

Naphthionic Acid + α-Naphthol Sulpho Acid N.W.



Wool in an acid bath is dyed red which resists the action of acids and alkalis.

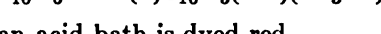
Fast Red.

Naphthionic Acid + β-Naphthol Sulpho Acid S.

Wool in an acid bath is dyed red.

Fast Red D.

Naphthionic Acid + β-Naphthol Disulpho Acid R.



Wool and silk in an acid bath are dyed a bluish red. The dye equalizes well and is fast to acids and alkalis and moderately fast to light.

NAME. COMPONENTS COUPLED BY DIAZOTIZING

New Coccine.

Naphthionic Acid + β-Naphthol Disulpho Acid G.

$NaO_3SC_{10}H_6N{=}N(1)C_{10}H_4(OH)(SO_3Na)_2$ 2:6:8

Dyes wool and silk a scarlet which resists light and is fast to acids and alkalis.

Ponceau 6R.

Naphthionic Acid + β-Naphthol Trisulpho Acid

$NaO_3SC_{10}H_6N{=}N(1)C_{10}H_3(OH)(SO_3Na)_3$ 2:3:6:8

Wool in an acid bath is dyed a bluish red that is fast to light.

Double Brilliant Scarlet G.

β-Naphthylamine Sulpho Acid Br + β-Naphthol

$HaO_3S(6)C_{10}H_6(2)N{=}N(1)C_{10}H_6(OH)$ 2

Dyes wool a yellowish red: it is fast to washing upon silk.

Crumpsall Yellow.

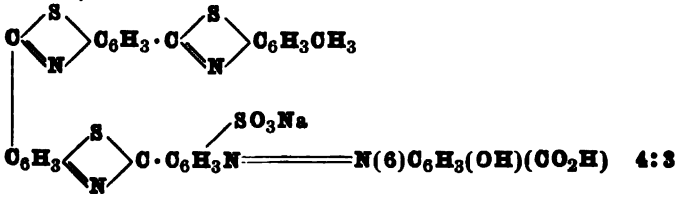
β-Naphthylamine Disulpho Acid G. + Salicylic Acid

6:8 $(NaO_3S)_2C_{10}H_5(2)N{=}N(6)C_6H_3(OH)(CO_2H)$ 3:4

Wool alone and wool mordanted with chromium salts is dyed yellow.

Cotton Yellow R.

Primuline + Salicylic Aci



Dyes cotton without a mordant in a bath containing Glauber's salt. Fast to light and the action of acids and soap.

NAME. COMPONENTS COUPLED BY DIAZOTIZING

Diamond Yellow R.

o-Aminobenzoic Acid + Salicylic Acid

$HO_2CC_6H_4N{=}N(1)C_6H_3(OH)(CO_2H)$ 4:3

Wool mordanted with chromium salts is dyed a reddish yellow which is fast to light and milling.

Diamond Yellow G.

m-Aminobenzoic Acid + Salicylic Acid

$HO_2CC_6H_4N{=}N(1)C_6H_3(CO_2H)(OH)$ 3:4

Dyes wool mordanted with chromium salts a greener shade of yellow than diamond yellow R.

Indoine Blue R.

Safranine + β-Naphthol

$S{-}N{=}N(1)C_{10}H_6OH$ 2

Cotton mordanted or unmordanted is dyed a very fast shade of indigo blue.

Rosophenine S.G.

Primuline + α-Naphthol Sulpho Acid N.W.

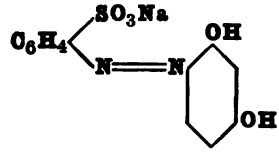
$P{-}N{=}N(2)C_{10}H_5(OH)(SO_3Na)$ 1:4

Cotton is dyed without a mordant from pale rose shades to deep carmine red.

DISAZO DYES: PRIMARY

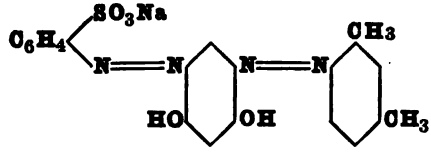
This class of dyes includes those whose molecules contain two azo groups (—N=N—). The dyes are formed in two steps. A substance containing an amino group is diazotized and coupled with a molecule of an amine or a phenol. Then upon this product a second molecule of a diazotized substance is allowed to act. Of course it will attach itself to another carbon atom than that with which the first diazotized substance united.

For example, sulphanilic acid is diazotized and coupled with resorcin, forming resorcin yellow, as shown below:



Resorcin yellow (monazo dye)

If *m*-xylidine be diazotized and allowed to act upon the monazo dye resorcin yellow, it will unite with it, forming a disazo dye resorcin brown, which appears when completed as follows:



Resorcin brown (disazo dye)

The following list is made up of dyes formed in a similar manner:

Leather Brown.

p-Amino acetanilid
p-Amino acetanilid } *m*-Phenylene diamine

Dyes leather and unmordanted jute brown.

Terra Cotta F.

Primuline
Naphthionic acid } *m*-Phenylene diamine

Cotton is dyed without a mordant in weakly alkaline bath containing Glauber's salt a fast brown.

Fast Brown.

Naphthionic acid
Naphthionic acid } Resorcin

Wool in an acid bath is dyed brown which is fast to acids and alkalis.

Fast Brown G.

Sulphanilic acid
Sulphanilic acid } > α-Naphthol

Wool in an acid bath is dyed brown.

Palatine Black.

Sulphanilic acid coupled in acid solution
α-Naphthylamine coupled in alkaline solution } > 1.8-Aminonaphthol-4-sulpho acid

Wool and silk are dyed black.

Disazo Dyes: Secondary

In this division of the disazo dyes an aminoazo dye is diazotized and then combined with various amines and phenols. This class contains many dyes of importance in wool dyeing. An illustration which is typical in the method of formation is the following:

Aniline yellow is one of the simplest monazo dyes and has the formula given below:

$$C_6H_5N{=}NC_6H_4NH_2 \cdot HCl$$

Aniline yellow (monazo dye)

By diazotizing this, there is obtained the diazotized aniline yellow:

$$C_6H_5N{=}NC_6H_4N{=}NCl$$

which combines with β-naphthol, forming Sudan III.:

$$\underset{\text{Diazotized aniline yellow}}{C_6H_5N{=}NC_6H_4N{=}NCl} + \underset{\beta\text{-naphthol}}{HC_{10}H_6OH} =$$

$$C_6H_5N{=}NC_6H_4N{=}N(1)C_{10}H_6OH\ 2. + HCl$$

Sudan III

The following dyes are members of this class:

Cloth Red G. Aminoazobenzene α-Naphthol sulpho acid N.W. (1:4).

Ponceau 5R. Aminoazobenzene + β-Naphthol trisulpho acid 2:3:6:8.

Cloth Red 3B. Aminoazotoluene + Ethyl β-Naphthylamine-δ-monosulpho acid (2:5).

Crocein B. Aminoazotoluene + α-Naphthol disulpho acid Sch. (1:4:8).

Cloth Red B. Aminoazotoluene + α-Naphthol sulpho acid N.W. (1:4).

Bordeaux B.X. Aminoazoxylene + β-Naphthol sulpho acid S. (2:6).

Orchil Red A. Aminoazoxylene + β-Naphthol disulpho acid R. (2:3:6).

Cloth Scarlet G. Aminoazobenzene sulpho acid + β-Naphthol.

Ponceau 4R.B. Aminoazobenzene sulpho acid + β-Naphthol sulpho acid B. (2:8).

Crocien Scarlet O. (extra). Aminoazobenzene disulpho acid + β-Naphthol sulpho acid B. (2:8).

Fast Ponceau 2B. Aminoazobenzene disulpho acid + β-Naphthol disulpho acid R. (2:3:6).

Crocein Scarlet 8B. Aminoazotoluene sulpho acid + β-Naphthol sulpho acid B. (2:8).

Fast Violet (reddish). Sulphanilic acid azo-α-Naphthylamine + β-Naphthol sulpho acid S. (2:6).

Anthracite Black B. α-Naphthylamine disulpho acid azo-α-Naphthylamine + Diphenyl-*m*-phenylene diamine.

Naphthylamine Black D. α-Naphthylamine disulpho acid azo-Naphthylamine + α-Naphthylamine.

Diamond Green. Aminosalicylic acid azo-α-Naphthylamine + Dioxynaphthalene monosulpho acid S. (1:8:4).

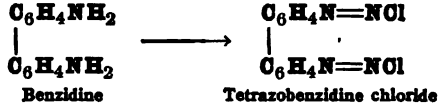
Diamond Black F. Aminosalicylic acid azo-α-Naphthylamine + α-Naphthol sulpho acid N.W. (1:4).

Janus Red. *m*-Aminophenyl-trimethyl-ammonium + *m*-Toluidine + β-Naphthol.

Direct Disazo Dyes from Benzidine and its Homologues

The dyes formed from benzidine and its homologues, as previously stated in this chapter, by diazotization and coupling with amines and phenols can be applied to cotton without the aid of a mordant. They are the so-called direct dyes.

Benzidine possesses two amino groups and both are easily diazotized by the aid of sodium nitrite and an acid, with the result shown below:



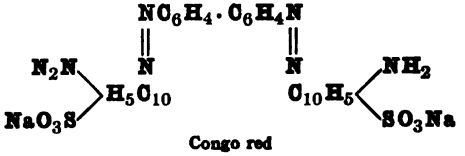
Benzidine — Tetrazobenzidine chloride

This product may now become coupled with two molecules of an amine, two molecules of a phenol or one amine and one phenol. Furthermore, the amines may be unlike and the phenols may be unlike, thus widening the scope of this reaction and producing a large number of dyes. The number is further increased by the homologues of benzidine, e.g., tolidine, $CH_3(H_2N)C_6H_3 \cdot C_6H_3(NH_2)CH_3$, having the same power of producing new dyes.

The coupling action of tetrazobenzidine chloride is not equally rapid for both molecules of the second component. The first molecule reacts at once; the complete coupling of the second molecule is much slower, sometimes requiring several days.

If the second components are alike, the dyes are known as simple benzidine dyes: if they are unlike, mixed benzidine dyes result.

When, for example, the tetrazobenzidine chloride unites with two molecules of sodium naphthionate and the acid product neutralized by an alkali, a red dye called Congo red is formed—the first direct dye whose discovery introduced the manufacture of this valuable class of colors:



Congo red

A few of the important dyes of this class are listed below, showing the primary substance (a *p*-diamine) which is doubly diazotized as a starting point and the secondary components which unite with it to form the dye:

Brilliant Congo G.

Benzidine
- (1) β-Naphthylamine disulpho acid 2:3:6.
- (1) β-Naphthylamine monosulpho acid, 2:6.

Diamine Fast Red F.

Benzidine
- (1) Salicylic acid, 4:5.
- (1) β-Aminonaphthol sulpho acid, 2:8:6, in acid solution.

Benzopurpurin B.

Tolidine
- (1) β-Naphthylamine sulpho acid Br, 2:6.
- (1) β-Naphthylamine sulpho acid Br, 2:6.

Rosazurine B.

Tolidine
- (1) Ethyl-β-Naphthylamine δ-sulpho acid, 2:7.
- (1) Ethyl-β-Naphthylamine δ-sulpho acid, 2:7.

Azo Blue.

Tolidine
- (2) α-Naphthol sulpho acid N.W., 1:4.
- (2) α-Naphthol sulpho acid, N.W. 1:4.

Benzoazurine G.

Dianisidine
- (2) α-Naphthol sulpho acid N.W., 1:4.
- (2) α-Naphthol sulpho acid N.W., 1:4.

Pyramine Orange 3G.

Benzidine
- (2) *m*-Phenylene diamine disulpho acid, 1:3:4:6.
- (4) Nitro-*m*-phenylene diamine, 1:3:6.

Diamine Black B.H.

Benzidine
- (7) Aminonaphthol sulpho acid γ, 2:8:6 (in alkaline solution).
- (7) Aminonaphthol sulpho acid H., 1·8.3:6 (in alkaline solution).

Benzopurpurin 10B.

Dianisidine
- (2) Aminonaphthalene sulpho acid, 1:4.
- (2) Aminonaphthalene sulpho acid, 1:4.

Chicago Blue 6B.

Dianisidine
- (7) Aminonaphthol disulpho acid S., 1:8:2:4.
- (7) Aminonaphthol disulpho acid S., 1:8:2:4.

Carbazol Yellow.

Diaminocarbazol
- (1) Salicylic acid, 4:5.
- (1) Salicylic acid, 4:5.

Diamine Sky Blue.

Dianisidine
- (7) Aminonaphthol disulpho acid H., 1:8:3:6 (in alkaline solution).
- (7) Aminonaphthol disulpho acid H., 1:8:3:6 (in alkaline solution).

Naphthylene Red.

1:5 Diamino-naphthylene
- (2) Naphthionic acid.
- (2) Naphthionic acid.

Chrysophenine.

Diaminostilbene disulpho acid
- (4) Phenol, 1.
- (4) Phenetol, 1.

St. Denis Red.

Diamino-azoxytoluene
- (2) α-Naphthol sulpho acid, N.W. 1:4.
- (2) α-Naphthol sulpho acid N.W., 1:4.

Trisazo Dyes

In all dyes of this class will be found three double nitrogen or azo (—N=N—) groups. They all become implanted by successive diazotizing reactions in producing the finished molecule of the dye. For a disazo dye to become a trisazo dye it is necessary that the former contain an amino group

which may be diazotized ready for coupling with another component. The following example will make this clear: Benzidine, $C_6H_4(NH_2)_2$, with its two amino groups diazotized may become coupled to two molecules of amines or phenols. If in one of the second components an amino group is present this may be diazotized and coupled with a third component to form a trisazo dye:

Oxamine Violet G.R.F.

Benzidine → β-Naphthol disulpho acid R., 2:3:6.
Benzidine → Phenylene-*m*-diamine oxamic acid + *m*-Phenylene diamine.

Benzo Olive.

Benzidine → Salicylic acid.
Benzidine → α-Naphthylamine + Amino naphthol disulpho acid H., 1:8:3:6.

Diamine Bronze G.

Benzidine → Salicylic acid.
Benzidine → Aminonaphthol disulpho acid H. + *m*-Phenylene diamine.

Columbia Black R.

Tolidine → Aminonaphthol disulpho acid 2R., 2:8:3:6, + *m*-Toluylene diamine.
Tolidine → *m*-Toluylene diamine.

Benzo Black Blue R.

Tolidine → α-Naphthol sulpho acid N.W., 1:4.
Tolidine → α-Naphthylamine + α-Naphthol sulpho acid N.W.

Benzo Black Blue G.

Benzidine disulpho acid → α-Naphthylamine + α-Naphthol sulpho acid N.W., 1:4.
Benzidine disulpho acid → α-Naphthol sulpho acid N.W.

Alizarine Yellow F. S.

Rosaniline → Salicylic acid.
Rosaniline → Salicylic acid.
Rosaniline → Salicylic acid.

Columbia Black F.B.

p-Phenylene diamine → *α*-Naphthylamine sulpho acid (Cleve), 1:3.
p-Phenylene diamine → Aminonaphthol sulpho acid G. + *m*-Phenylene diamine, 2:8:6.

A trisazo dye may also be formed from a benzidine dye even when no amino group appears in either of the second components ready for diazotizing. In this case one of the second components must be of such a nature that a separately prepared diazo compound will couple with it.

The following dyes exhibit this method of formation:

Congo Brown G.

Benzidine → Salicylic acid.
Benzidine → Resorcin.
Sulphanilic acid

Here the second component resorcin, containing no amino group, is still able to react with diazotized sulphanilic acid, the third diazo group being brought into the reaction by the last-named component:

Diamine Green G.

Benzidine → Salicylic acid.
Benzidine → Aminonaphthol sulpho acid H.
p-nitraniline

Columbia Green.

Benzidine → Salicylic acid.
Benzidine → Aminonaphthol sulpho acid S., 1:8:4.
Sulphanilic acid

Congo Brown R.

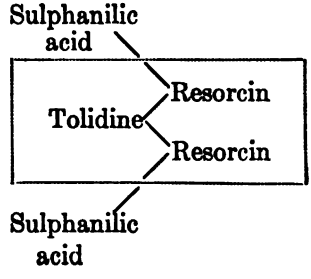
Benzidine → Salicylic acid.
Benzidine → Resorcin.
α-Naphthylamine sulpho acid L., 1:5.

Tetrakisazo Dyes

Four azo groups (—N=N—) characterize this class of dyes. The molecules are the most complex of the azo dyes but are more easily comprehended by regarding them as made of components simpler than the finished dye held together by the same binding azo groups throughout.

They are frequently produced on the fabric. An illustration is furnished by Hessian brown M.M., which is made by allowing two molecules of diazotized sulphanilic acid to act upon a substance which is already a disazo dye carrying two azo groups known as pyramidal brown T.:

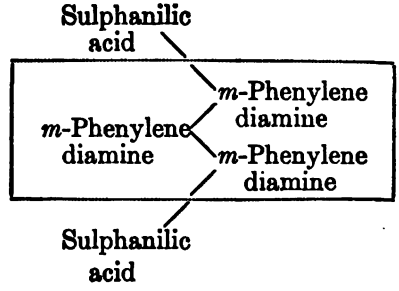
Hessian Brown M.M.



The initial disazo dye pyramidal brown T. is shown within the dotted line: the gain in thus converting one brown dye into another brown dye is depth of shade and greater fastness.

Other dyes of this class are:

Benzo Brown G.



The initial disazo dye in this instance is Bismarck brown, which is inclosed in the dotted line.

Mekong Yellow G.

Benzidine — Salicylic acid.
Dioxydiphenyl methane
Benzidine — Salicylic acid

Two molecules of benzidine are diazotized and each coupled to a molecule of sulphanilic acid; then these two molecules thus prepared join themselves to the central molecule of dioxydiphenyl methane.

The following dye is similarly constituted; the final step being the union of two molecules of the intermediate product to dioxydiphenyl methane:

Azo orange R.

Tolidine — Naphthionic acid.
Dioxydiphenyl methane.
Tolidine — Naphthionic acid.

Mekong Yellow R.

Tolidine — Salicylic acid.
Dioxydiphenyl methane.
Tolidine — Salicylic acid.

CHAPTER IX

THE TWELVE FOOD COLORS[1]

In the processes of preserving many fruits and vegetables, and the products made from them, the natural colors are often diminished to such an extent as to give them a deceptive appearance of inferior quality. To remedy this, artificial colors are used to restore as far as possible the original shades.

The advent of coal-tar colors of intense power and brilliance, more durable and cheaper than most vegetable colors, naturally led to their use in foods and beverages. Had they been harmless, little objection would have been made against them, save where a dishonest merchant or manufacturer might hope by their aid to conceal real inferiority in his goods.

These colors are not all harmless. Some of them are dangerous poisons and others harmless in themselves are dangerous from metallic salts contained therein, or because of the arsenic they have acquired from the sulphuric acid directly or indirectly employed in some stages of their manufacture.

The result has been that after long and careful consideration the number of coal-tar colors for foods and beverages has been limited by the government to seven. These were selected both because they are harmless in themselves and their manufacture can be so conducted as to produce a pure product, excluding contamination with arsenic or poisonous metallic salts and avoiding the retention of the raw materials or any foreign matter whatever, and their patents have expired, leaving their manufacture open to all competitors.

The arsenic contamination comes from the sulphuric acid employed. As the U. S. Pharmacopœia requires that sulphuric

[1] Permitted in foods and beverages by the U. S. Government.

The names of the five new colors permitted by the Government are given at the end of this chapter.

acid shall not contain more than one part of arsenic in 100,000, and as sulphuric acid can be obtained in large quantities containing only one part of arsenic in 500,000 and without increase in the price, the manufacture of these colors free from arsenic offers no special difficulties.

These seven colors and mixtures of them are regarded as ample for producing any desired shade in foods, beverages, condiments or confectionery. The seven permitted colors are:

Red	107.	**Amaranth.**
	56.	**Ponceau 3R.**
	517.	**Erythrosine.**
Orange	85.	**Orange I.**
Yellow	4.	**Naphthol Yellow S.**
Green	435.	**Light Green S.F. Yellowish.**
Blue	692.	**Indigo Disulpho Acid.**

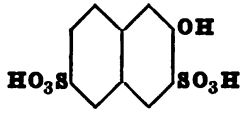
They all belong to the class of acid colors. All except erythrosine owe their acid properties to the salt-forming sulpho acid group, (—SO_3H). Erythrosine contains the salt-forming groups, (—CO·OH), and (—OH).

The seven colors are further classified as:

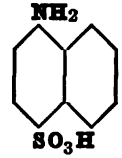
Acid Colors	**Amaranth.** **Orange I.** **Ponceau 3R.**	**Azo Colors.**
	Naphthol Yellow S.	**Nitro Color.**
	Light Green S. F. (Yellowish).	**Triphenyl methane Color.**
	Indigo Disulpho Acid.	**Indigo Color.**
	Erythrosine.	**Pyronine Color.**

Amaranth appears in commerce as a reddish brown powder which dissolves in water with a fuchsine red color. If hydrochloric acid is added to the solution no change occurs; but it turns dark when sodium hydroxide is added. It dissolves in strong sulphuric acid with a violet color which turns bluish violet on addition of water. Is is not easily soluble in alcohol.

This color is prepared by diazotizing naphthionic acid and coupling this product with β-naphthol disulpho acid R. These two ingredients and the finished color have the structure assigned below:

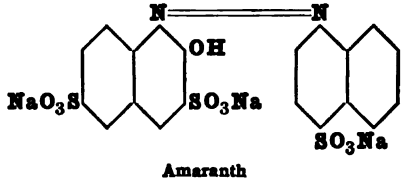


β-Naphthol-disulpho acid R.



Naphthionic acid

The sodium salt of the product of the above diazotizing and coupling actions is amaranth:

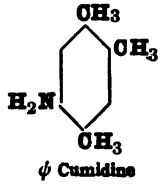


Amaranth

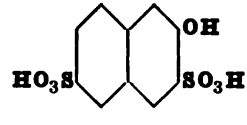
Amaranth is not affected by acids and alkalies, and yields a bluish red which resists to a fair degree the action of light.

Ponceau 3R. forms a dark red powder. In water it dissolves easily with a cherry red color, but in alcohol it dissolves with difficulty to a yellowish red color. No change in the solution occurs when hydrochloric acid is added, but a yellow precipitate falls when sodium hydroxide is used. A cherry red solution is formed with strong sulphuric acid and the addition of water causes no change.

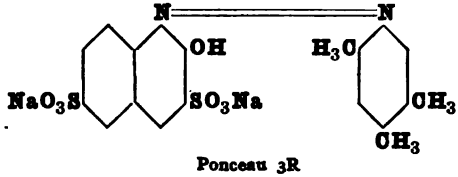
Ponceau 3R. results from the action of diazotized ψ-cumidine upon β-naphthol disulpho acid R. The commercial color is the sodium salt of this product:



ψ Cumidine



β-Naphthol disulpho acid R



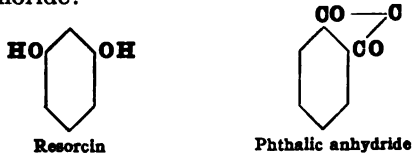
Ponceau 3R

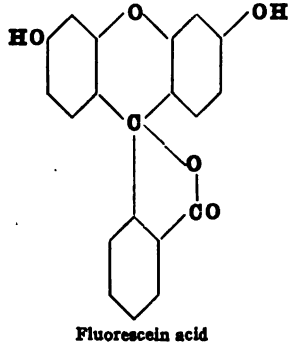
Erythrosine is the only one of the seven colors containing iodine. It is a yellowish brown powder which forms a cherry red solution in water. Unlike some other dyes of the pyronine class, its solution exhibits no fluorescence.

From the solution a brownish yellow precipitate falls on the addition of hydrochloric acid, while no change is caused by sodium hydroxide: in solutions of certain strength a red precipitate falls which redissolves in an excess of water.

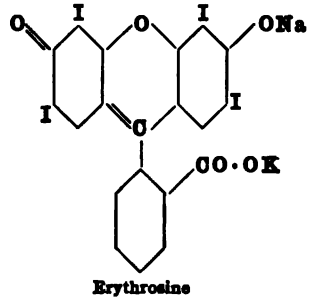
When the color dissolves in strong sulphuric acid a brownish yellow solution results, and this by warming evolves iodine vapors. Addition of water to the solution in sulphuric acid causes a yellow precipitate.

Erythrosine may be prepared by treating fluoresceine with iodine in alcoholic or aqueous solution. The fluoresceine itself is made by heating together two molecules of resorcin and one molecule of phthalic anhydride to 190–200° C. alone or with zinc chloride:





When this has been enriched by four iodine atoms and further has been neutralized to form the sodium or potassium salt, it becomes erythrosine:



Erythrosine

Orange I. is a reddish brown powder which communicates an orange red color to water and an orange shade to alcohol. In both liquids it dissolves easily.

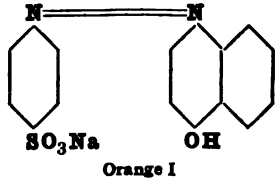
A brown precipitate forms when hydrochloric acid is added and change of color to cherry red follows the addition of sodium hydroxide. A violet solution in strong sulphuric becomes red brown by dilution with water.

Orange I. is made by diazotizing sulphanilic acid and coupling the product with α-naphthol. The sodium salt of this product is orange I.

Orange I. may be contaminated with the poisonous orange **II.** as an impurity:

Sulphanilic acid

α-Naphthol



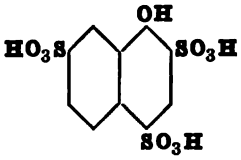
Orange I

Naphthol Yellow S. comes into the market as a bright yellow or orange yellow powder. It burns with a yellow flame accompanied by scintillation. The powder dissolves easily in water with a yellow color.

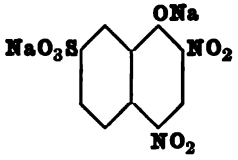
Hydrochloric acid turns the solution to a brighter shade of yellow, but no precipitate is formed. Very different effects are observed upon adding the potassium and sodium hydroxides; the former causes a flocculent precipitate in exceedingly dilute solutions while the latter has no effect. The solution in strong sulphuric acid is a yellow which becomes brighter as water is added.

Naphthol yellow S. may be made by the action of nitric acid upon 1-naphthol 2·4·7 trisulpho acid. The potassium or sodium salt of the product forms the color.

Naphthol yellow S. may contain the poisonous Martius yellow, either as an impurity or an adulteration.



1-Naphthol 2.4.7. disulpho acid



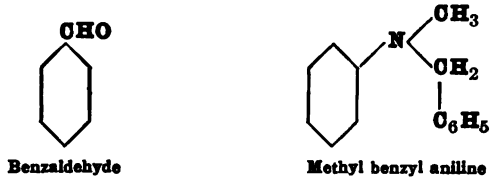
Naphthol yellow S

Wool and silk may be dyed yellow from an acid bath.

Light Green S.F. (yellowish) is a bright green lusterless powder which dissolves in both water and alcohol with a green color. The solution becomes yellowish brown on addition of hydrochloric acid. Sodium hydroxide bleaches the solution, and then causes a turbidity with violet color.

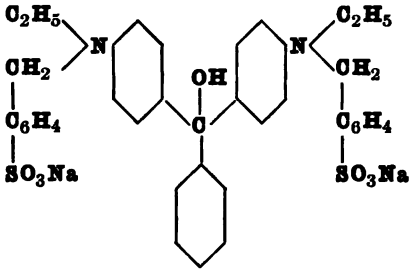
Neither barium chloride nor picric acid cause a precipitate. The yellow solution in strong sulphuric acid becomes slowly green on dilution with water.

Light green S.F. (yellowish) is manufactured by bringing together benzaldehyde and methyl benzyl aniline. The condensation product thus formed is sulphonated by sulphuric acid and then oxidized: neutralization then forms the salt, which is the color.



Benzaldehyde

Methyl benzyl aniline

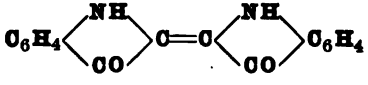


Light green S.F. (yellowish)

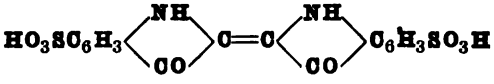
Indigo Disulpho Acid is a fine powder of blue color, which dissolves easily in water with a blue color. A bluish violet effect is caused by adding hydrochloric acid to its solution, but this changes to blue again on diluting with water. Sodium hydroxide develops an olive green which remains on dilution. The bluish violet which it communicates to strong sulphuric acid is again turned blue as water is added.

Indigo disulpho acid is one of the products which results from treating either natural or artificial indigo with fuming sulphuric acid. The blue insoluble indigo is enriched with two sulpho groups by the process and thereby becomes soluble.

Indigo disulpho acid may be contaminated with indigo monosulpho acid:



Indigo blue (insoluble)



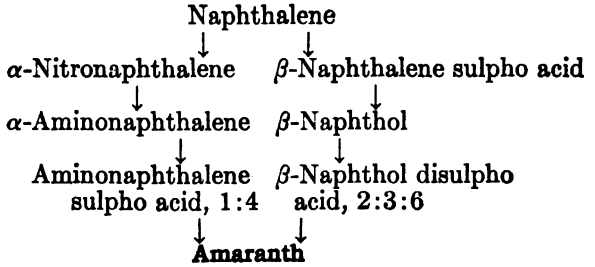
Indigo disulpho acid (soluble)

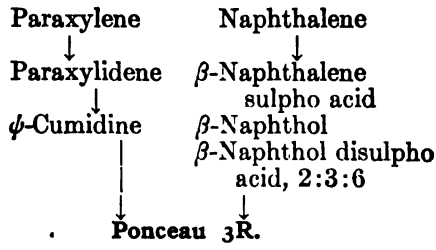
The process of manufacture may begin at the coal-tar products themselves or at any of the intermediate products, or even with the finished color as it is found in commerce itself. In this last instance the manufacture would consist in purification of the commercial color sold as a dye for fabrics to render it pure for the coloring of foods. In the eye of the law the one who purifies crude colors is also a manufacturer, as well as he who fabricates the crude dye itself from the simpler products of coal-tar distillation.

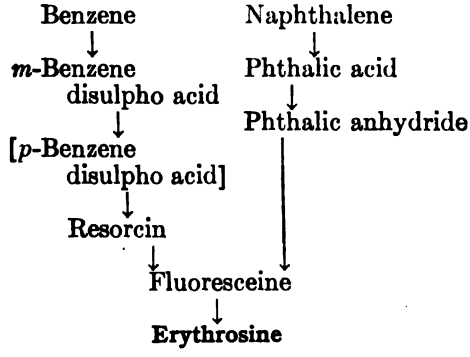
It will be seen at a glance from the following scheme of primary and intermediate substances needed for the making of these seven colors, that the primary substances are few; further, that excepting indigo disulpho acid only four primary substances are used, viz.: benzene, toluene, paraxylene, and naphthalene, and that naphthalene, which can readily be obtained of a high degree of purity, enters into the manufacture of five out of the seven food colors.

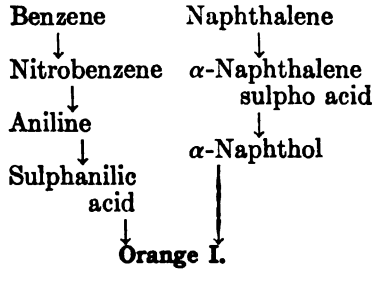
The finished product must not be contaminated with any of the intermediate substances used in the manufacture, nor with any subsidiary products which may be formed or with any impurities brought in by the inorganic chemicals employed during manufacture.

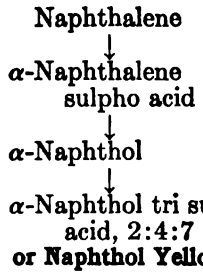
The following scheme shows what are the primary and intermediate coal-tar products used in the manufacture of the seven food colors:

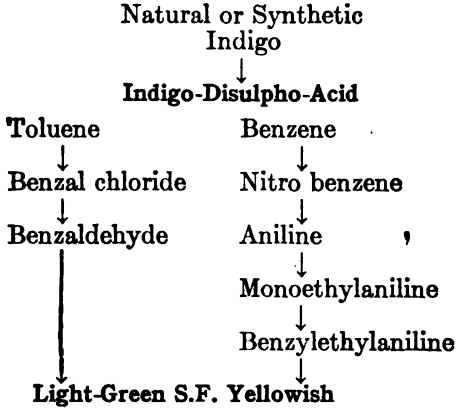



Paraxylene
Naphthalene
Paraxylidene
β-Naphthalene sulpho acid
ψ-Cumidine
β-Naphthol
β-Naphthol disulpho acid, 2:3:6
Ponceau 3R.


Benzene
Naphthalene
m-Benzene disulpho acid
Phthalic acid
Phthalic anhydride
[p-Benzene disulpho acid]
Resorcin
Fluoresceine
Erythrosine


Benzene
Naphthalene
Nitrobenzene
α-Naphthalene sulpho acid
Aniline
α-Naphthol
Sulphanilic acid
Orange I.


Naphthalene
α-Naphthalene sulpho acid
α-Naphthol
α-Naphthol tri sulpho acid, 2:4:7
or Naphthol Yellow S.



TEXT OF INSTRUCTIONS OF THE U. S. GOVERNMENT FOR MANUFACTURERS AND CONSUMERS OF FOOD COLORS.

FOOD INSPECTION DECISION 76

Issued July 13, 1907.

List of Dyes Permitted Pending Further Investigation

The following list of dyes has been recommended in the decision for use in foods and foodstuffs, pending further investigation and announcement of its results:

Red Shades:

107. **Amaranth.**
56. **Ponceau 3R.**
517. **Erythrosine.**

Orange Shades:

85. **Orange I.**

Yellow Shades:

4. **Naphthol Yellow S.**

Green Shades:

435. **Light-Green S.F. Yellowish.**

Blue Shades:

692. **Indigo Disulpho Acid.**

The decision further states that these coal-tar dyes must be made specifically for use in foods and bear a guarantee from

the manufacturer that they are free from subsidiary products and represent the actual compound whose name they bear.

The following statement is necessary in order to illustrate the principles guiding the Department of Agriculture in framing this portion of the decision:

An extended study of the large number of so-called coal-tar dyes which are now in use for the coloring of foods and foodstuffs has been necessary to arrive at a conclusion concerning the restriction, if any, which may be placed on their use, and the Department acknowledges the very efficient aid rendered during the course of this study by Dr. Bernhard C. Hesse, of New York city. Doctor Hesse has had an extended experience in this subject through his long association with the leading dyestuff manufacturers in Germany. Since severing his connection with them he has given his time largely to expert work along this line.

The literature on this subject is very unsatisfactory as to what coal-tar products are used, and is not to be depended upon, because of the equivocal nature of the terminology employed. It is impossible to reduce this terminology to an unequivocal and definite basis for the great majority of such coal-tar colors.

It was impracticable to go to all those in the United States who use coal-tar dyes in food products and obtain specimens of the coal-tar colors so used. This is true not only because of the large number of such users and their wide geographical distribution, but also because of the reluctance which would undoubtedly be encountered among many such users to disclose the nature of the products employed by them.

The sources of coal-tar materials are limited in number, however. By reference to the book entitled "A Systematic Survey of the Organic Coloring Matters," by Arthur G. Green, published in 1904, on pages 9 and 10 thereof, it will be seen that there are thirty-seven different concerns in the world engaged in the manufacture of coal-tar materials.

Therefore a canvass of these sources for such coal-tar coloring matters as, in their judgment, or in their business practice, they regard as proper for use in food products, seemed the best

mode of obtaining a knowledge of the field of the coal-tar colors here in question.

Communication was had, therefore, with thirteen manufacturers of coal-tar colors in an endeavor to obtain from them a list of such coal-tar colors as in their judgment or business practice were deemed suitable for use in food products. When this co-operation was established, request was also made for information as to the composition of the coal-tar samples submitted, and in order to avoid confusion samples were to be identified by reference to the "Systematic Survey of the Organic Coloring Matters," by Green, in which each coal-tar color has its own number. This information is necessary to reduce the terminology to a common and unequivocal basis. The thirteen manufacturers, or their accredited agents, with whom communication was held probably represent from 85 to 90 per cent of the total dyestuff output of the world.

In order to make provision for the twenty-four makers on the list in the Green tables, and not included in the thirteen makers consulted, a request for samples was made from two New York city houses who themselves import coal-tar colors from sources other than the above, for use in food products. Their products must fairly represent any output not represented by the thirteen makers above mentioned.

The question of the choice of dyes for the coloring of foodstuffs has been decided on the basis of those dyes which have been submitted by the manufacturers or their accredited agents, but it was impossible to consider any dyes when the manufacturer or the accredited selling agent was unwilling to state unequivocally what the dyes submitted were, so that they could be identified chemically.

When those interested in placing dyestuffs on the market for the coloring of food have shown unwillingness to give information of this kind as to what they sell, and by thus selling, recommend, the burden of proof as to the harmlessness of such dyes lies with them, and until such proofs are adduced, the use of such dyes should be inhibited.

With this knowledge of the specific nature of the dyes recommended, the Department has made a study of those

concerning which there has been the greatest unanimity of opinion among the manufacturers or their agents as to their fitness; and in the cases where such dyes have been studied as to their physiological action, and the reports have been favorable, they have been included in the tentative list proposed in the food inspection decision herewith.

This tentative list of dyes includes a wide range of colors sufficient for all legitimate purposes. Among them are none which are patented, so that their manufacture is open to all interested in the dye industry.

One point must be particularly emphasized regarding the use of these dyes, namely, the need for the manufacturer's guarantee of purity. It is the manufacturer above all who knows the exact nature of his dyestuffs, and if he is willing to sell his colors for use in foodstuffs he should be willing to guarantee that the dyes really are what they are represented to be, that they are not mixtures, and that they do not contain harmful impurities.

In order further to minimize the possibility of harmful impurities existing in these dyes, it has been thought necessary to require a further examination by competent experts, a certificate from whom is necessary, stating that the dyes in question are what they are represented to be.

FOOD INSPECTION DECISION 76—*Continued*

[So much of it as relates to colors]

The use of any dye, harmless or otherwise, to color or stain a food in a manner whereby damage or inferiority is concealed is specifically prohibited by law. The use in food for any purpose of any mineral dye or any coal-tar dye, except those coal-tar dyes hereinafter listed, will be grounds for prosecution. Pending further investigations now under way and the announcement thereof, the coal-tar dyes hereinafter named, made specifically for use in foods, and which bear a guaranty from the manufacturer that they are free from subsidiary products and represent the actual substance the name of which they bear, may be used in foods. In every case a certificate that the dye in question has been tested by competent

experts and found to be free from harmful constituents must be filed with the Secretary of Agriculture and approved by him.

The following coal-tar dyes which may be used in this manner are given numbers, the numbers preceding the names referring to the number of the dye in question as listed in A. G. Green's edition of the Schultz-Julius "Systematic Survey of the Organic Coloring Matters," published in 1904.

The list is as follows:

RED SHADES:

107. Amaranth.
56. Ponceau 3R.
517. Erythrosine.

ORANGE SHADES:

85. Orange I.

YELLOW SHADES:

4. Naphthol Yellow-S.

GREEN SHADES:

435. Light Green S.F. Yellowish.

BLUE SHADES:

692. Indigo Disulpho Acid.

Each of these colors shall be free from any coloring matter other than the one specified and shall not contain any contamination due to imperfect or incomplete manufacture.

H. W. WILEY, FREDERICK L. DUNLAP, GEO. P. MCCABE,
Board of Food and Drug Inspection.

Approved: JAMES WILSON, *Secretary of Agriculture;* GEO. B. CORTELYOU, *Secretary of the Treasury;* OSCAR STRAUSS, *Secretary of Commerce and Labor.*

WASHINGTON, D.C., June 18, 1907.

FOOD INSPECTION DECISION 77

Issued September 25, 1907

CERTIFICATE AND CONTROL OF DYES PERMISSIBLE FOR USE IN COLORING FOODS AND FOODSTUFFS

The Department of Agriculture is in receipt of a large number of inquiries concerning the interpretation to be put on that portion of F. I. D. 76 which refers to coal-tar dyes not inhibited for use in coloring foods and foodstuffs.

The term " manufacturer," as used in F. I. D. 76 and in the present decision, applies to a person or company responsible for the purification of the crude or raw dye for the purpose of placing it in a condition fit for use in foods and foodstuffs; or to the accredited selling agent in the United States of such person or company. Such accredited agent must file, on behalf of his foreign principal, if the latter does not file it, a manufacturer's certificate, and it will be considered that the responsibility for such certificate will rest upon the accredited agent and not upon the foreign principal.

For each permitted dye two certificates must be filed by the manufacturer, the first to be known as the " Foundation certificate," the second known as the " Manufacturer's certificate." It is suggested that the foundation certificate be in the following form:

FOUNDATION CERTIFICATE

I, ..., the undersigned, residing at .....
(Street address.)
in the city of....., county of....., State of..
....., hereby certify under oath that I have personally examined and tested for ....., of ....., county
(Full name of concern.) (City.)
of....., State of ....., the material known as ....., which corresponds to the coloring matter numbered ..... in A. G. Green's Edition (1904) of the Schultz-Julius "Systematic Survey of the Organic Coloring Matters," and of which a one (1) pound sample marked ..... is herewith submitted. I have found the said material to consist of that coloring matter only, to be free from harmful constituents, and not to contain any contamination due to imperfect or incomplete manufacture.

(*Here insert a complete statement of all the tests applied to determine:*

A. *Identity.*

B. *Absence of*

a. *Mineral or metallic poisons.*

b. *Harmful organic constituents.*

c. *Contamination due to improper or incomplete manufacture.*

Special attention should be given to setting forth fully the quantities or volume of each material and reagent employed, its strength or concentration, temperature, duration of treatment, limits of delicacy of tests employed, and any other information that is necessary to enable others to repeat

accurately and correctly all the work herein referred to and thus arrive at identical results. For each test performed, state what conclusions are drawn from it and why.)

.....
(Signature of chemist making the examination.)

CERTIFICATION.

For the manufacturer's certificate the following form is suggested:

MANUFACTURER'S CERTIFICATE

I, ..., the undersigned, a resident of the United States, doing business at ....., in the city of .....
(Street address.)
....., county of ....., State of.....
under the style of ....., do hereby certify under oath
(Full name of concern.)
that I am the manufacturer of the material known at .....,
which corresponds to the coloring matter numbered ..... in the 1904 Green Edition of the Schultz-Julius Tables, of which the accompanying foundation certificate, signed by ....., the examining chemist, is the report of an analysis of a fair, average sample drawn from a total batch of ..... pounds.

.....
(Signature of manufacturer.)

CERTIFICATION.

The foundation certificate must be filed with the Secretary of Agriculture at the time the first request is made of the Secretary to use any or all of the permitted dyes for coloring foods and foodstuffs.

The following form of supplemental certificate is suggested in those cases where a manufacturer desires to apply for permission to place on the market a new batch of a coal-tar dye, which dye has already had a foundation certificate and a manufacturer's certificate filed for it:

SUPPLEMENTAL CERTIFICATE

I, ..., the undersigned, residing at,.....,
(Street address.)
in the city of ....., county of ....., State of
....., hereby certify under oath that I have personally examined and tested for ....., of .....,
(Full name of concern.) (City.)
county of ....., State of ....., the material known as
....., which corresponds to the coloring matter numbered ..... in A. G. Green's Edition (1904) of the Schultz-Julius

"Systematic Survey of the Organic Coloring Matters," of which a one (1) pound sample marked ..... is herewith submitted, and I have found it to consist of that coloring matter only and to be free from harmful constituents and not to contain any contamination due to imperfect or incomplete manufacture.

This examination was conducted in strict accordance with the detailed scheme of examination fully set forth in the foundation certificate filed .....
(Date.)

.....
(Signature of chemist.)

CERTIFICATION.

This supplemental certificate should likewise be accompanied by the same type of manufacturer's certificate as is described above.

When the certificates filed with the Department of Agriculture are found to be satisfactory, a "lot number" will be assigned to each batch, which lot number shall apply to that batch alone and to no other batch of the same color.

According to F. I. D. 76, the seven permitted coal-tar dyes therein named, made specifically for use in foods, may be used in foods provided they bear a *guaranty* from the manufacturer that they are free from subsidiary products and represent the actual substance the name of which they bear. The guaranty herein considered shall be applied as follows:

Each package sold by the manufacturer should bear the legend "Part of Certified Lot Number ....." The foundation certificate, as well as the corresponding supplemental certificate, does not apply to any certified dye beyond the package originally prepared by the one establishing this certificate. If such a package be broken and the dye therein contained be repacked, the repacked dye, except as hereinafter provided, becomes an uncertified dye, and as such is inhibited.

There is no objection on the part of the Department of Agriculture to mixtures made from these permitted and certified dyes, by those who have filed certificates with the Department, but one (1) pound samples of such mixtures, and the trade name under which each mixture is sold, must be sent to the Secretary of Agriculture, and no such trade name or keyed modification thereof may be used for any other mixture.

The exact formula—that is, the true names as well as the numbers assigned to the original package and the proportions of the ingredients used—should be deposited with the Secretary of Agriculture, but such formula need not appear on the label; in lieu of which may appear the legend "Made from Certified Lots Number ..... and Number ....," etc. If the packages of these mixtures bearing this legend be broken and repacked, the mixture becomes, except as hereinafter provided, an uncertified one, and hence its use is inhibited; that is, the guaranty of the manufacturer shall extend only to the packages prepared by himself and only for so long as they remain in the unbroken form. Whenever new lots of previously established mixtures are made, making use of new certified straight dyes therein, thus necessitating a change in the label, 1-pound samples of the new mixtures should be sent to the Secretary of Agriculture.

The term "competent experts" as used in F. I. D. 76 applies to those who, by reason of their training and experience, are able to examine coal-tar coloring matter to ascertain its identity and to determine the absence of foreign matter not properly belonging to the product, which, if present, renders the substance unfit for use in food products.

The term "batch" as used above is such a quantity of the product as has undergone the same treatment at the same time and the same place as a unit and not otherwise—that is, the lot for one purification.

Those to whom certification is given with respect to their dyes and a lot number assigned should control the sale of such batches so that they may account to the Department of Agriculture by inspection of their books or otherwise for the destination and disposal of each batch.

Those using these certified dyes in the preparation of foods and foodstuffs must be in a position to substantiate the fact that the dyes so used were of a properly certified character.

There is no guaranty on the part of the Department of Agriculture that because the tests described in any foundation certificate have once been accepted, the permanency of such acceptance is assured.

In those cases where a package of a straight dye or a mixture of such dyes, bearing proper labels to the effect that they are of a certified lot or lots, is broken and repacked in still smaller lots, or treated with solvents, mixed, etc., the person or company so treating these dyes must stand sponsor for their integrity. This may be accomplished by submitting a statement to the Secretary of Agriculture as follows:

SECONDARY CERTIFICATE

I, ..., residing at ....., do hereby
(Full address.)
certify under oath that I have repacked ..... lbs. of certified lot (or lots) ..... purchased from ....., of ..... This repacking has been accomplished in the following fashion: .....
.....
.....
(Full description of what has been done with the lot or lots.)

.....
(Name.)

CERTIFICATION.

On presentation of this certified form, properly filled out, to the Secretary of Agriculture, a lot number will be assigned, which number should be used in labeling according to the methods already described. If, for example, a portion of lot number "127" is repacked in smaller packages, the lot number "127 A" will be assigned to this repacked dye, to enable the Department to follow this into consumption if necessary and still trace it back to the person by whom the dye was originaly certified.

H. W. WILEY, F. L. DUNLAP, GEO. P. MCCABE, *Board of Food and Drug Inspection.*

Approved: JAMES WILSON, *Secretary of Agriculture.*

WASHINGTON, D. C., Sept. 16, 1909.

FOOD INSPECTION DECISION 106

Issued March 25, 1909

AMENDMENT TO FOOD INSPECTION DECISION NO. 77

(A definition of the terms "Batch" and "Mixtures" as used therein.)

The definition of the term "batch" as given on page 4, lines 12 to 14 of Food Inspection Decision 77, is hereby

extended to include also the contents of any one package, cask, or other container holding 500 pounds or less of dye, even though the contents of such package, cask, or container has not undergone the same treatment at the same time and the same place as a unit.

The word " mixtures " as used on page 3, line 15 from the bottom, and following, of Food Inspection Decision 77 is hereby declared to mean not only such mixtures as consist wholly of certified coal-tar dyes, but also those which contain one or more certified coal-tar dyes (and no other coal-tar dye or dyes) in combination with other components, constituents, or ingredients not coal-tar dyes, which other components, constituents, or ingredients are in and of themselves or in the combination used harmless and not detrimental to health or are not prohibited for use in food products; the exact formula of such mixtures, including all of the components, constituents, or ingredients, or other parts of the mixture, together with a statement of the total weight of mixture so made, must be deposited with the Secretary of Agriculture and a one (1) pound sample thereof must be sent to the Secretary of Agriculture, but such formula need not appear on the label; in lieu of which may appear the legend " Made from certified lots Number ..... and Number ....., etc.," and no mention need be made of any constituent or constituents other than of the certified coal-tar dyes employed.

H. W. WILEY, F. L. DUNLAP, GEO. P. MCCABE, *Board of Food and Drug Inspection.*

Approved: JAMES WILSON, *Secretary of Agriculture.*

WASHINGTON, D. C., March 19, 1909.

FOOD INSPECTION DECISION 117

Issued May 3, 1910

THE USE OF CERTIFED COLORS

Food Inspection Decision No. 76, published July 13, 1907, gives a list of seven coal-tar dyes, which may, without objection from the Department of Agriculture, be used in foods until further notice. Food Inspection Decision No. 77, published

September 25, 1907, provides for the certification of dyes. Food Inspection Decision No. 77 was amended March 25, 1909, by Food Inspection Decision No. 106. Some manufacturers have succeeded in producing the seven colors, under the conditions outlined in Food Inspection Decision No. 77. Certified dyes are now on the market. Certified dyes may be used in foods without objection by the Department of Agriculture, provided the use of the dye in food does not conceal damage or inferiority. If damage or inferiority be concealed by the use of the dye, the food is adulterated.

Uncertified coal-tar dyes are likely to contain arsenic and other poisonous material, which, when used in food, may render such food injurious to health and, therefore, adulterated under the law.

In all cases where foods subject to the provisions of the Food and Drugs Act of June 30, 1906, are found colored with dyes which contain either arsenic or other poisonous or deleterious ingredient which may render such foods injurious to health, the cases will be reported to the Department of Justice and prosecutions had.

The Department is in possession of facts which show that there are so-called vegetable colors on the market which contain excessive quantities of arsenic, heavy metals, and contaminations due to imperfect or incomplete manufacture. While the Department has raised no objection to the use of vegetable colors, per se, yet the use of colors even of vegetable origin, open to the objection of excessive arsenic, etc., should not be used for coloring food products.

F. L. DUNLAP, GEO. P. MCCABE, *Board of Food and Drug Inspection.*

Approved: JAMES WILSON, *Secretary of Agriculture*

WASHINGTON, D. C., April 7, 1909.

Note. The five new colors authorized by the Government for use in foods and beverages are Tatrazine, Sudan I, Butter Yellow, Yellow A.B. and Yellow O.B.

CHAPTER X

THE PYRONINES

THE pyronines form a class of dyes which exhibit yellow, yellowish red, rose red, bluish, and violet red, and blue colors that produce most brilliant and beautiful effects. They often possess a splendid fluorescence, especially when dyed upon silk, less frequently on wool, and seldom upon cotton, except with the occasional use of an oil mordant.

The chief raw material which comes directly from coal tar is naphthalene, which is converted into phthalic acid and then into phthalic anhydride, in order to be combined with the phenols and amino phenols to produce the bases of the various pyronine dyes.

The pyronines comprise a small subclass of basic dyes called pyronines and a larger class known as phthaleins: latter class contains further the eosines and rhodamines.

THE PYRONINES

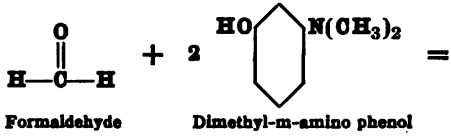
This class of dyes differs from the phthaleins in containing only two benzene rings, while the latter has three. The benzene rings contain side-chains of amino, (—NH_2), and hydroxyl, (—OH), groups which appear, e.g., in the form of dimethyl-*m*-amino phenol, $C_6H_4(OH)N(CH_3)_2$.

By the use of aliphatic aldehydes and acids, the phenols may be condensed into substances which on the subsequent elimination of water and oxidation are converted into dyes.

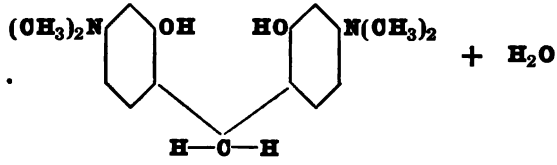
Pyronine G. (1889) appears in crystals of a green lustre which impart a red color to water with a yellowish fluorescence. The first step in its preparation is the union of formaldehyde with dimethyl-*m*-

Dimethyl-m-amino phenol

amino phenol. These substances unite with the separation of a molecule of water:

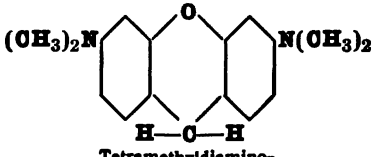


Formaldehyde Dimethyl-m-amino phenol



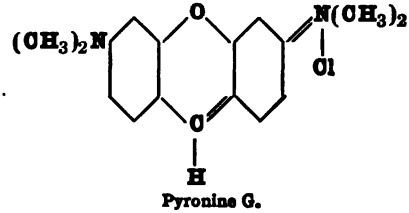
Tetramethyldiamino-dioxydiphenylmethane

In this product it will be noticed that the hydroxyl groups are in the ortho position in reference to the methane cabon atom, and the next step involves the further separation of another molecule of water and a union of the rings by the remaining oxygen atom—an anhydrization characteristic of the pyronine and phthalein dyes. The result appears in the following formula, and it is brought about by the action of concentrated sulphuric acid:



Tetramethyldiamino-diphenylmethane oxide

By oxidation and the formation of a salt, the dye is produced with the structure as follows:



Pyronine G.

Hydrochloric acid turns the red aqueous solution to a bright orange, while sodium hydroxide causes a pale red precipitate. It dissolves in strong sulphuric acid with a reddish yellow color which turns to red when the solution is diluted with water.

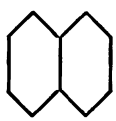
Silk, wool, and also cotton mordanted with tannin and tartar emetic are dyed a carmine red which is moderately fast to light and even faster to soap.

The Phthaleins

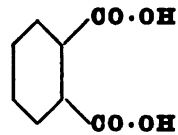
This class of dyes takes its name from phthalic anhydride, $C_{10}H_6(CO)_2O$, which is easily formed from phthalic acid by distillation. In its turn phthalic acid is made by the oxidation of naphthalene, naphthol, or dinitronaphthol.

Thus, naphthalene, one of the largest individual constituents of coal tar, is the basis of the manufacture of this particularly brilliant class of dyes.

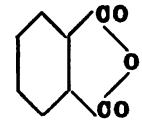
Out of the three phthalic acids theoretically possible, the one obtained by the oxidation of naphthalene or its derivatives is that which has the two carboxyl groups attached to neighboring carbon atoms, known as orthophthalic acid, of the following constitution:



Naphthalene

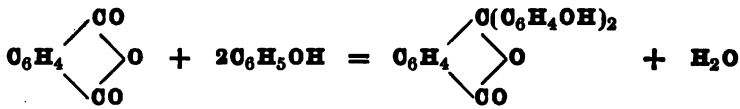


Phthalic acid



Phthalic anhydride

The discovery of the first dye from phthalic anhydride was made in 1871 by Adolph Baeyer. He found that, on heating phthalic anhydride with a phenol and some substance, e.g., fused anhydrous, zinc chloride, to take up water, a condensation takes place that may be represented as follows:



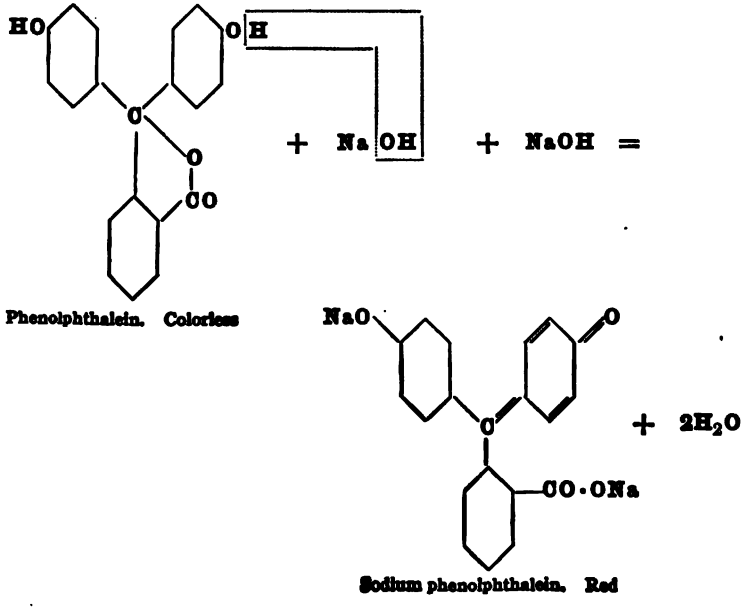
Phthalic anhydride Phenol Phenolphthalein

Contrary to expectation the middle oxygen of the phthalic anhydride is not the one which is replaced by the two phenol radicles through loss of a hydrogen atom from each, but one of the oxygens of a carbonyl group; thus an unsymmetrical formula results.

The hydrogen atom which is removed from each molecule of phenol stands opposite to the hydroxyl group or occupies the para position. From the method of formation, a lactone ring remains unbroken in this molecule of phenolphthalein, and this was supposed to be the cause of the development of color in all the various phthaleins to be described.

As the substance itself has no color at all and only develops its characteristic red color on adding an alkali to form a salt, and as the lactone ring is now regarded as broken when the salt of the substance is formed, the ring formation can no longer be regarded as the potential source of color possibilities.

What is supposed to take place when, for example, the sodium salt of phenolphthalein is formed may be represented as follows:

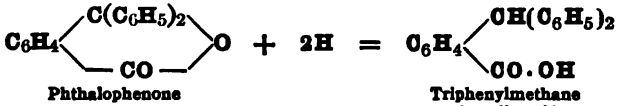


As the alkali salt is formed, the lactone ring is broken and a hydrogen atom is lost from a phenol hydroxyl causing a rearrangement of valence for that phenol residue into a quinone formation.

Quinone formation

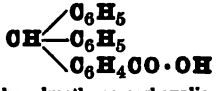
The intimate connection between the phthaleins and the triphenylmethane compounds is evident from the fact that, by the action of nascent hydrogen, the phthaleins are reduced to phthalins, which are derivatives of triphenylmethane. During this reduction the lactone ring is broken with the formation of a carboxyl group.

The simplest example of such a reduction is best shown by the simplest phthalein, called phthalophenone. It lacks the two hydroxyls of phenolphthalein, otherwise it is similarly constituted.



Phthalophenone — Triphenylmethane carboxylic acid

When the latter compound is written in the following form the resemblance is at once apparent:



Triphenylmethane carboxylic acid

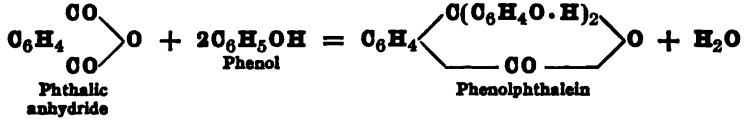
This substance loses CO_2 by dry distillation and is changed into triphenylmethane $CH(C_6H_5)_3$.

The transformation of phthalophenone into triphenylmethane already shown, and now farther into phenolphathlein, completes the proof of connection between the phthaleins and triphenylmethane. This latter conversion is carried out by first treating phthalophenone with dilute nitric acid, which introduces two nitro groups into the molecule, forming dinitrophthalophenone. By reduction, the nitro groups are changed

into amino groups and by diazotizing these amino groups and boiling with acid, two hydroxyl groups become fixed where the original nitro groups entered and the product is phenolphthalein.

Phenolphthalein (1871) occurs in the form of yellow crystals or a buff-colored powder, which will not dissolve in water, but is easily soluble in alcohol.

It is made by heating together the solid white phthalic anhydride and crystalline carbolic acid in molecular proportions, fused zinc chloride or concentrated sulphuric acid being added to take up the water formed.



When alkalies are added to an aqueous solution to which a few drops of the alcoholic solution have been added, an intense red is produced. Upon this action depends its use as an indicator in volumetric analysis. As shown above, the lactone ring is broken when the alkali salt is formed which produces the red color. An excess of strong alkali causes decoloration. It is chiefly used as an indicator in quantitative analysis.

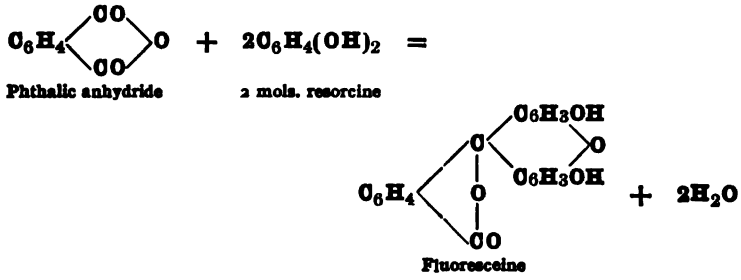
Fluoresceine (1871), **(Uranine)**, is a dye which in the form of its sodium salt exhibits a yellow color in its aqueous solution with a most intense yellowish-green fluorescence.

The coloring power of such a solution is very great, one part of uranine giving a definite pale green fluorescence to 16 million parts of water. Whole rivers may be colored for a time with a kilogram of the dye. The courses of rivers that are partly subterranean have been determined by thus coloring the water. By this means it has been proved that an underground connection exists between the Danube and a small river called the Aach, which flows into Lake Constance.

Fluoresceine is formed by heating together molecular proportions of phthalic anhydride and resorcin, $C_6H_4(OH)_2$, to 195°–200°, until no steam is given off and the mass has

become solid. The cooled melt is pulverized and it serves for the manufacture of the eosines.

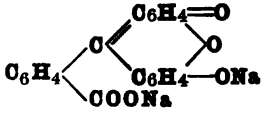
The formation of fluoresceine may be represented thus:



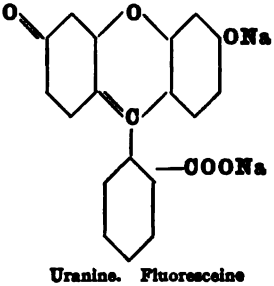
Phthalic anhydride — 2 mols. resorcine — Fluoresceine

The fluoresceine is a brown powder which will not dissolve in water but does dissolve in alcohol. On adding fluoresceine to an alkaline solution it dissolves and forms the sodium salt called uranine, and it is this compound which is so intensely fluorescent in dilute solution. In a concentrated solution it does not show fluorescence.

Uranine. As the salt of the fluoresceine or uranine is formed, the lactone ring is broken and a quinoid rearrangement produced which is shown in the formulas below:



Uranine. Fluoresceine



Uranine. Fluoresceine

Uranine is used in dyeing yellow upon silk and employed to some extent in printing upon wool.

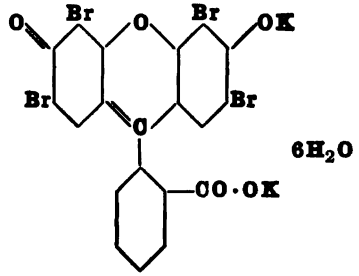
A yellow precipitate is thrown down from an aqueous solution of the dye by hydrochloric acid, while caustic soda changes the color and causes it so show a darker green fluorescence.

Uranine forms insoluble lakes with lead and silver which, from being non-poisonous, may be used for coloring toys and rubber.

Eosine (1874), (Eosine Yellowish, Eosine G.G.F., Eosine G., Eosine extra, Eosine A., Eosine D.H.). Fluoresceine is capable of yielding one of the most brilliantly beautiful dyes by further modification. It was discovered by Heinrich Caro in 1874 that bromine would be absorbed by fluoresceine, which thereby became transformed into a beautiful red dye. To this dye he gave the name of Eosine (Eos, flush of dawn), because of its beauty and brilliant effect when dyed upon silk.

The measure of appreciation bestowed upon the new color is shown by the initial price of $100 per pound which it commanded. This did not prevent its immediate use for dyeing silk. It stimulated, at the same time, the production of a whole series of dyestuffs. All of them are of exceeding beauty, though unfortunately more or less fugitive in character. It appears in the market as reddish blue crystals or a brownish red powder soluble in water with a bluish red color. A green fluorescence is exhibited by the dilute solution.

It is prepared by treating fluoresceine in either alcohol or water with bromine when four atoms of bromine become fixed in the molecule, two in each resorcine nucleus. The pure potassium salt crystallizes with six molecules of water with the formula, $C_{20}H_6Br_4O_5K_2 6H_2O$, and has the following structure:

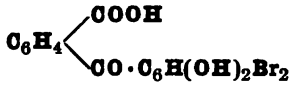


Eosine

The Structure of Eosine

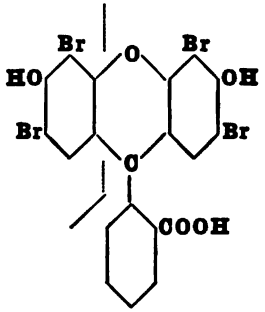
In the molecule of eosine there are three benzene rings, one furnished by the phthalic anhydride, the other two by the resorcine residues. The hydroxyl groups must be in the resorcine portions of the dye molecule because they were in the resorcine at the start; but their position in reference to the methane carbon remains to be determined; then, also, the position of the four bromine atoms—whether they enter the resorcine or phthalic acid residues or are distributed in both.

The first step in this solution was taken by Baeyer when he decomposed the eosine molecule with boiling caustic soda. This produced a substance whose composition and constitution were already known. This substance was dibromo dioxybenzoyl benzoic acid of the following constitution:

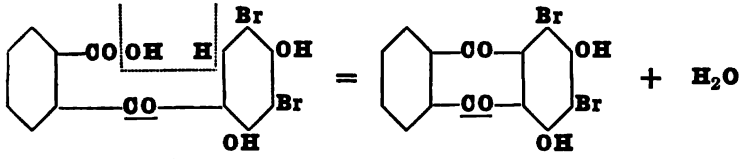


Dibromo dioxybenzoyl benzoic acid

The eosine molecule in order to produce this must have broken along the dotted line of the formula below:



Now the hydroxyl and bromine atoms will retain in this acid formed the same positions they occupied in the eosine molecule. By the use of fuming sulphuric acid, G. Heller decomposed this acid. Water was separated and a dibromodioxy anthraquinone was formed. The positions of the hydroxyls and bromine atoms in this product are well established and the only possible method of its formation seems to be as follows:

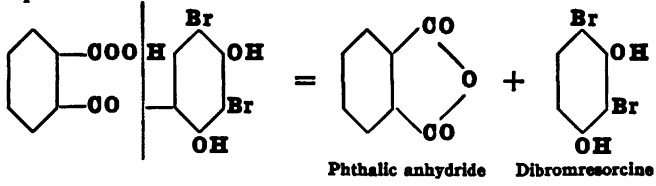


Dibromo dioxybenzoyl benzoic acid — Dibromodioxy anthraquinone

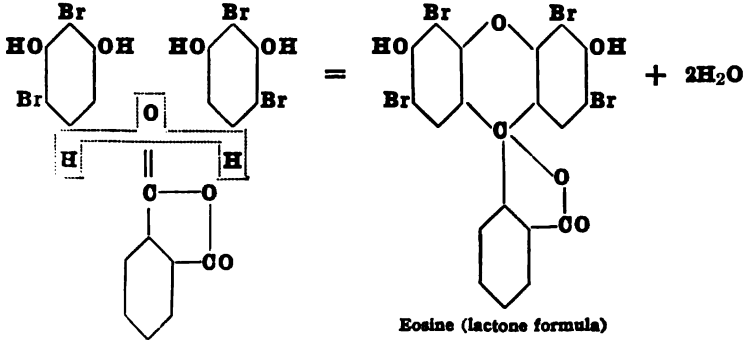
In this latter substance, the positions of the hydroxyls and bromines are known, i.e., the two hydroxyls occupy the para and ortho positions in reference to the carbon atom underscored; while the two corresponding meta positions are taken by the bromines.

By this nothing has been proved in regard to the hydroxyls and bromines of the other resorcine radical which was eliminated in the formation by the boiling caustic soda, of the dibromo dioxybenzoyl benzoic acid.

Richard Meyer by a single brilliant experiment has proved that the other resorcine radical has the same constitution as the first. He melted pure dibromo dioxybenzoyl benzoic acid and obtained phthalic anhydride and eosine. The progressive steps of this beautiful reaction may be seen from the equations:



Phthalic anhydride — Dibromresorcine



Eosine (lactone formula)

This demonstration clears up the question of the position of all four hydroxyls and all four bromines; incidentally proving also the position of the hydroxyls in the molecule of fluoresceine.

The entrance of the four bromine atoms has the effect of changing the yellow of fluoresceine to the pinkish red of eosine.

Eosine dissolves in 2 or 3 parts of water. Yellow insoluble flocks are formed by hydrochloric acid. The color becomes darker on adding caustic soda and a yellowish red product separates.

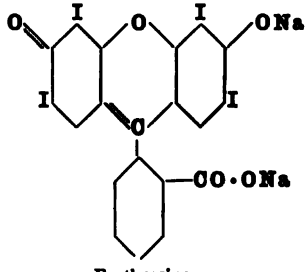
Wool and silk are dyed a pinkish red from a weakly acid bath: silk exhibits a yellowish red fluorescence. It is also employed for coloring paper and varnishes. An imitation vermilion is produced by using a colored lake of this dye with red lead.

It combines with oxides, forming insoluble or slightly soluble lakes. They may be prepared by mixing aqueous solutions of the metallic salts with eosine, when the bright colored precipitates are thrown down. If alcohol be added to the dilute aqueous solution of eosine, its flourescence is increased.

Eosine Orange and Eosine 3G. are mixtures of dibrom and tetrabrom fluoresceine.

Erythrosine (1876), (Erythrosine B., Erythrosine D., Pyrosin B., Rose B., Soluble Primrose, Eosine J., Eosine Bluish, Iodoeosine, Dianthine B.), is an iodine derivative of fluoresceine. It contains four atoms of iodine in place of the four bromine atoms of eosine.

The method of preparation is the same as for eosine, using iodine in place of bromine. The four bromine atoms on entering fluoresceine change its yellow color to the pinkish red of eosine, and when the four iodines enter, the yellow is changed to a bluish red. The structure of the sodium salt is:



Erythrosine

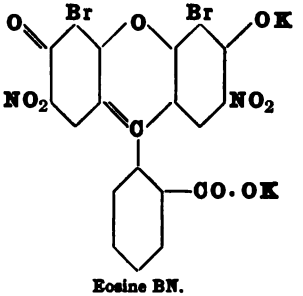
The potassium salt is also a commercial form of the dye. The dyestuff itself is a brown powder, which imparts a cherry red color to its solution in water. The solution fails to show any fluorescence.

A brownish yellow precipitate falls on adding hydrochloric acid. A soluble red precipitate also falls on adding caustic soda.

Wool and cotton that have mordanted with alum are dyed a bluish red. Erythrosine is also used in paper manufacture and in photography.

Eosine B.N. (1875), **Methyl Eosine, Safrosine, Eosine Scarlet B., Eosine B., Scarlet J., J.J., or V., Eosine D.H.V., Eosine Scarlet B.B. extra,** is a fluoresceine derivative which contains both bromine and nitro groups.

Either the dibrom fluoresceine may be nitrated in an aqueous solution or the dinitrofluoresceine may be brominated in an alcoholic solution. The resulting product is the same in either case and the potassium salt of the compound is shown below:



Eosine BN.
Alkali salt of dibromdinitro fluoresceine

The dyestuff is a brown crystalline powder which dissolves easily in water with a yellowish red color. If the solution is made dilute, it exhibits a weak green fluorescence.

Greenish yellow flocks separate from the solution when hydrochloric acid is added. No change occurs with caustic soda.

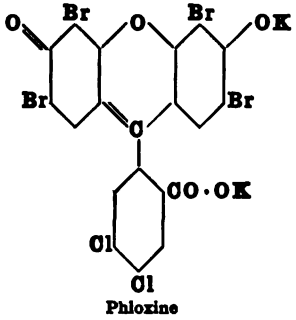
Silk and wool are dyed a bluish red, but of a somewhat darker shade than with erythrosine. This is more suitable for wool than for silk. The color is faster to light and milling than the majority of the eosines.

In comparison with eosine, which is a flouresceine containing four bromine atoms, this dye differs in having two of the four bromines replaced by two nitro groups and there results from this exchange a darkening of the color as well as greater fastness.

Phloxine (1875), (**Phloxine P., New Pink**), is a chlorine compound of eosine, but the chlorine is present in that part of the molecule derived from the phthalic acid used in its manufacture. In none of the dyes of this class so far discussed has any halogen appeared fixed in the benzene ring of the phthalic acid constituent of the dyestuff.

In phloxine, however, two chlorine atoms are fixed in the phthalic acid nucleus. These two chlorines are brought into this molecule by using dichlorphthalic acid instead of plain phthalic acid, and when this is melted with rescorcin, a dichlorfluoresceine results. By the action of bromine upon this latter product, four bromine atoms become fixed in the nuclei of the resorcin portion of the molecule. The potassium salt of this forms the phloxine of commerce.

The structural formula shows the relative positions of the bromine and chlorine atoms:



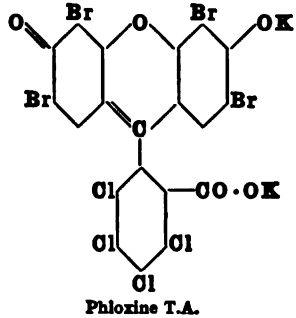
Phloxine

The commercial dyestuff is a brownish yellow powder, whose aqueous solution has a cherry red color, and also a greenish yellow fluorescence. Upon warming the solution with hydrochloric acid a brownish yellow precipitate is thrown down. Caustic soda turns the solution to a more bluish red.

Wool or silk is dyed from an acid bath a bluish red, without exhibiting any fluorescence, and the shade is bluer than that from erythrosine.

Cotton may be dyed, after first mordanting it with tin, lead, or aluminum salts.

Phloxine T.A. (1882). In the previous dye, phloxine, just described, two chlorine atoms are implanted in the phthalic acid nucleus of the molecule. By employing tetrachlor phthalic acid in place of dichlor phthalic acid, and combining this with resorcine a tetrachlor fluoresceine is produced with four chlorine atoms in the phthalic acid residue. When this compound is treated with bromine in alcoholic solution, four bromine atoms become fixed in the resorcine nuclei and the product is Phloxine T.A., which appears below as the sodium salt of commerce:



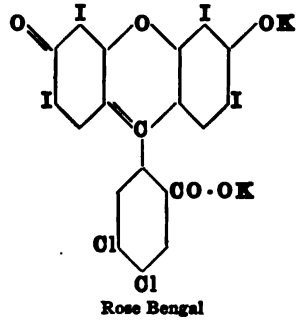
Phloxine T.A.

It will be noticed that this dye differs from phloxine in composition only by the two additional chlorine atoms. These have an influence in deepening the bluish shade of the red dye.

Phloxine T.A. has the appearance of brick red powder which dissolves in water with a bluish red color, and a slight dark green fluorescence. On the addition of hydrochloric acid decoloration takes place and a reddish flocculent precipitate appears. Caustic soda produces no change.

Rose Bengal (1875), (**Rose Bengal N., Rose Bengal A.T., Rose Bengal G.**), is a brilliant bluish red dye which is a direct derivative of dichlorfluoresceine. It is made from this substance by treating it with iodine, when four atoms of iodine

become fixed in the resorcine nuclei of the complex molecule. The two chlorine atoms are fixed in the phthalic acid nucleus. The potassium salt has the following structure:

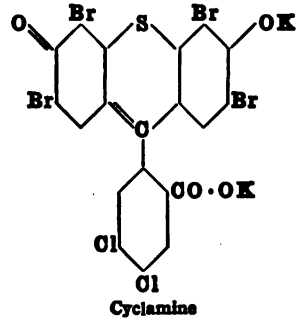


Rose Bengal

It forms a dark red powder, soluble in water with a cherry red color. No fluorescence is visible. A brown precipitate falls on adding hydrochloric acid. A carmine red soluble precipitate is caused by caustic soda.

Wool is dyed a bluish red without exhibiting any fluorescent effects.

Cyclamine (1889). If sodium sulphide is allowed to act upon dichlor fluoresceine, the sulphur changes place with an oxygen atom. It is supposed that the oxygen joining the resorcine nuclei is the one which is replaced by the sulphur. When this product is treated with bromine, four bromine atoms become attached to the resorcine rings and cyclamine is formed:



Cyclamine

In aqueous solution, cyclamine has a rosaniline red color without showing fluorescence. A reddish flocculent precipitate forms with hydrochloric acid. No change follows the addition of caustic soda.

Wool and silk are dyed a bluish red color from a neutral bath.

The Rhodamines

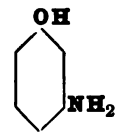
The pyronine dyes discussed to this point have been acid in character on account of the carboxyl group which each contains and, further, because of the phenolic hydroxyl group also present. The former is brought into the molecular structure by the phthalic anhydride and the latter by the resorcin employed in their manufacture.

If in the final product the phenolic hydroxyls are replaced by amino groups or by substituted amino groups, then there is a change in the dye molecule from an acid to a basic character. These dyes therefore form salts with acids.

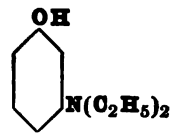
The rhodamines are consequently basic pyronines. Phenols already containing amino groups are employed in their preparation and communicate a basic character to the rhodamines, of which they become a constituent part.

Rhodamine B. (1887), (**Rhodamine O.**), differs from the preceding dyes of this class by containing amino groups. These communicate a basic character sufficient to cause it to dye cotton mordanted with tannin.

The amino groups are present in the metaminophenols which are constituents of the melt:



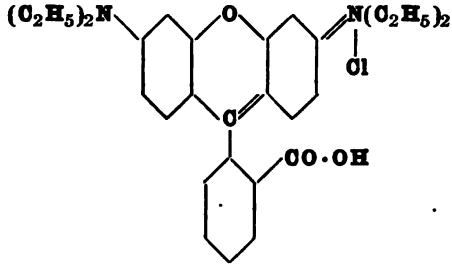
Metaminophenol



Diethylmetaminophenol

The diethyl derivative of metaminophenol is the compound usually employed. This is melted with phthalic anhydride and rhodamine B. results. It exceeds in bril-

liancy the splendid eosines. The hydrochloride salt of the dye is:

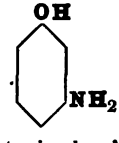


Rhodamine B.

Rhodamine B. (1887), **(Rhodamine O.)**, belongs to a series even more brilliantly beautiful than the eosines, though it is closely related to them and belong to the same class, viz., phthaleins. As the name suggests, it contains nitrogen in the form of an amino group. In this particular they differ from the eosines, and to this difference must be traced their greater brilliance.

The presence of the amino groups gives to an otherwise acid dye sufficient basic character to cause it to unite with cotton mordanted with tannic acid.

The amino groups are not implanted in a large molecule of a dye, but they are already fixed in each of two molecules of one of the constituents of the dye. This constituent is metaminophenol.



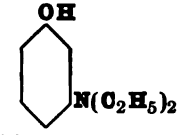
Metaminophenol

This substance may be made according to a process that starts with metasulphanilic acid, which is fused at 280–290° with twice its weight of caustic soda and a small amount of water. After dissolving the melt in water, it is made acid and then sodium carbonate is added.

Ether is used to extract the solution, and after the solvent

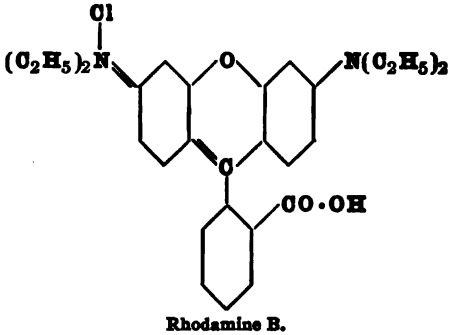
is distilled off, the crude product is purified by recrystallizing from water.

By choosing a diethylmetasulphanilic acid for the above fusion with caustic soda, a diethylmetaminophenol results.



Diethylmetaminophenol

It is this substance which on fusing with phthalic acid produces rhodamine B.



Rhodamine B.

This dye at once excited the attention of chemists by its brilliance and other properties and stimulated activity in this field of color chemistry which had lain dormant for several years.

Furthermore, it was welcomed by dyers, for it enabled them to secure handsome rose red shades upon cotton mordanted with tannin. Its basic character gives it this power.

Heretofore, with the acid eosines, it was necessary to develop on the cotton the undesirable lead lake of erythrosine. Afterward it was found to be a valuable dye for wool and silk.

The dye appears as a reddish violet powder or as green crystals, which are easily soluble in water with a bluish red

color. It also dissolves easily in alcohol, and even dilute solutions in this solvent exhibit strong fluorescence. Warming causes the fluorescence to disappear, but it reappears as the liquid cools.

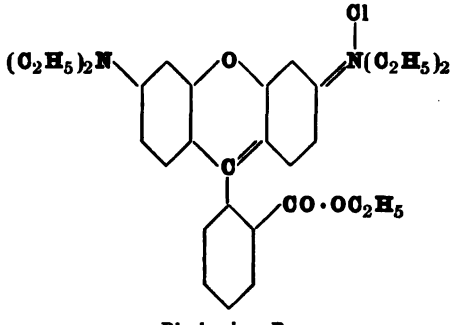
Hydrochloric acid in small amounts causes a gradual separation of the crystals of the hydrochloride, much hydrochloric acid turns the solution scarlet.

Caustic soda in small amounts causes no changes in the cold solution, but a rose red flocculent precipitate separates on warming. Large amounts of caustic soda cause the separation of red flocks even from a cold solution; on heating the odor of dimethylaniline is given off.

The dyeings of rhodamine B. are also esteemed for their fastness.

Rhodamine 3B. (1891), (**Anisoline**), is of a bluer shade of red than rhodamine B., and the cause of the increase of blue in the red dye is to be attributed to an ethyl group, which forms an ethereal salt or ester with the carboxyl group of rhodamine B.

The dye may be prepared by treating rhodamine B. with alcohol and conducting dry hydrochloric acid gas through the solution. A molecule of water is thereby eliminated and the ethyl group is united to the carboxyl group as shown below:



Rhodamine 3B.

By comparing this dye with **Rhodamine B.** it will be noticed that the additional ethyl group implanted in this dye was the

fifth, but that on replacing the hydrogen of the carboxyl group an ester is formed. We should thus expect that the acid character of the carboxyl group would be overcome, and that the basic character would at the same time be emphasized, and this is in fact what actually occurs.

The dyestuff forms a brownish red powder with a bronze lustre. Its aqueous solution shows a violet red color, with brownish red fluorescence when considerably diluted. In alcohol it dissolves, yielding a red solution with a purplish red fluorescence.

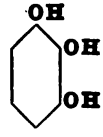
Hydrochloric acid turns the solution yellow, but on dilution it becomes red again.

No change takes place by adding caustic soda to a cold solution of the dye, but on heating saponification of the ester occurs and the original base of rhodamine B. is regenerated.

Silk, wool, and cotton that has been mordanted with tannic acid and tartar emetic are dyed a bluish shade of red of a bluer cast than rhodamine B.

Galleine (1871), (Alizarine Violet, Anthracene Violet), is a violet dye which appears in commerce as a voilet paste or as dark green crystalline powder of metallic lustre.

It is formed when phthalic anhydride is heated with pyrogallol $C_6H_3(OH)_3$. Atmosphere oxidation produces a quinone formation with the complex molecule.

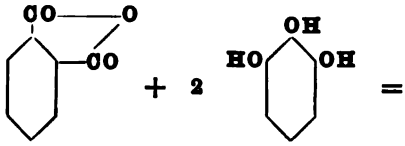


Pyrogallol

Pyrogallol may be made by heating gallic acid in an autoclave to 200–210°, or by heating gallic acid in glycerine in an open vessel at 190–200°, until no more carbonic acid is given off.

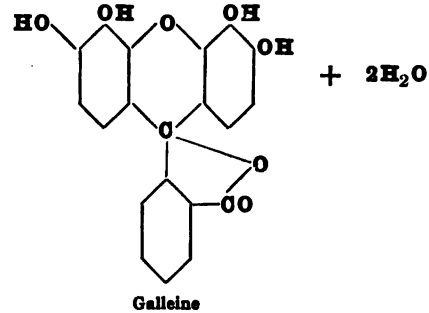
By either method a theoretical yield is obtained.

When this acts upon phthalic anhydride, the combination takes place as follows:



Phthalic anhydride

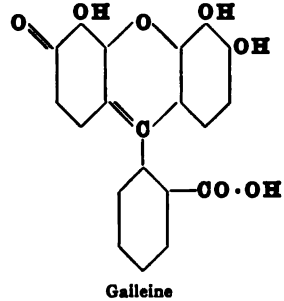
Pyrogallol



Galleine

The melt is boiled with water, dissolved in sodium carbonate, and after filtration acid is added, which precipitates the coloring matter.

Another constitution has been given to it as shown here:



Galleine

Galleine is a weak acid. In cold water it is slightly soluble, but it dissolves more easily in hot water with a scarlet color.

It dissolves easily in a solution of caustic alkali with a beau-

tiful blue color. The ammoniacal solution is violet and it yields violet precipitates with metallic salts. Hydrochloric acid turns the aqueous solution yellowish brown.

Galleine is a mordant dye and it is classed among the phthaleins because of its mode of formation rather than for its properties. In these it shows greater resemblance to the alizarine dyes. While the phthaleins almost all exhibit some shade of red, the lake of galleine is violet.

Its colored lakes possess a fastness far superior to the dyeings of the rest of the phthaleins.

Galleine produces upon wool mordanted with potassium bichromate and tartar emetic, dark shades of violet reputed for their beautiful "bloom." Fast shades of violet are dyed upon mordanted cotton. Lead mordants yield a beautiful grayish violet. Galleine is employed in cotton printing, in connection with the acetate of aluminum or chromium. By steaming, acetic acid is set free and the aluminum or chromium lake is fixed upon the fabric.

Though somewhat superseded as a dye, it is still extensively employed in the manufacture of coeruleine.

Coeruleine (1871), (**Alizarine Green, Anthracene Green**), is like **galleine** and for the same reason classed among the phthaleins, though like that dyestuff its properties recall those of the alizarine dyes.

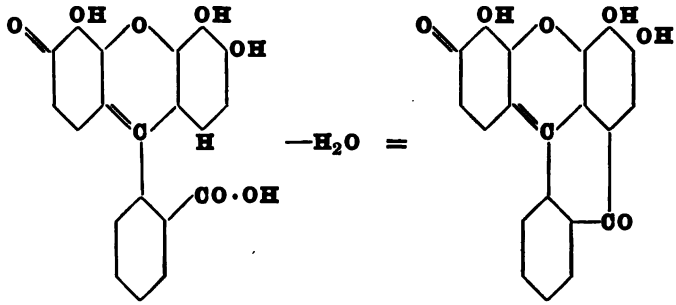
It is prepared from galleine by heating it to 200° with concentrated sulphuric acid. Twenty parts of acid to one of galleine are employed. The red color turns gradually to a brownish green. The cooled mixture on pouring into water throws down the dye as a bluish black powder which is washed and dried.

This powder by rubbing shows a metallic lustre.

It is almost insoluble in water, alcohol or ether; in glacial acetic acid it dissolves with a green color. The solution in concentrated sulphuric acid is olive green and that in hot aniline blue.

The action of sulphuric acid in the above operation is to extract a molecule of water from the molecule of galleine. Thus, by this removal and an internal rearrangement of the

molecule, a violet dye becomes a green one, whose composition is given:



Galleine Coeruleine

With sodium bisulphite the insoluble coeruleine combines to form a soluble compound called coeruleine S., which is easily decomposed again by boiling its solution or by the influence of either acids or alkalies, when sulphur dioxide is given off. Upon the formation of this soluble bisulphite compound depends its use in cotton printing. This soluble sodium bisulphite compound of coeruleine mixed with the acetate of aluminum or chromium is printed upon the fabric. Upon steaming the printed material, the bisulphite compound decomposes, acetic acid is evolved and the aluminum or chromium lake firmly attached to the fibre.

With the chromium mordant, dull olive greens are produced which equal in fastness the alizarine colors. The color is also fast to boiling soap or caustic alkalies.

Excellent results are secured with coeruleine on wool. Coeruleine may be used in conjunction with alizarine colors to produce a large variety of very fast shades.

The Acid Rhodamines

The **Rhodamines** differ from the **Eosines** in possessing a basic character because of the amino groups they contain.

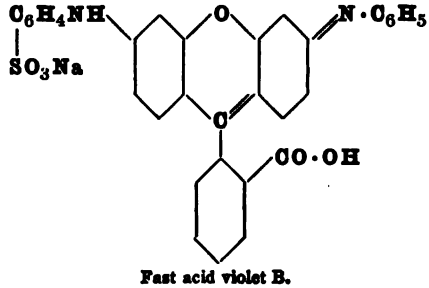
If, however, the rhodamines are treated with sulphuric acid, then the entrance of sulpho groups (SO_3H) into the molecule brings them into the class of acid dyes, since the acid

character now predominates in spite of the amino groups still present. They lose their value for cotton when losing their basic property, which enabled them to combine with the tannic acid mordant upon the cotton fibre.

They gain in value for wool and silk in their acquired acid properties and form fast dyes which equalize well during the dyeing operations.

Fast Acid Violet B. (1888), (Violamine B.). When aniline acts upon fluoresceine chloride, the aniline residues (C_6H_5NH—) become fixed in the positions which the hydroxyl groups did occupy. Thus the amino groups of the aniline convert the fluoresceine into a rhodamine and furthermore into phenylated rhodamine.

The sulphonation of the diphenyl rhodamine thus formed produces the acid dye whose constitution appears as follows:



Fast acid violet B.

Fast acid violet B. is a dark bluish violet powder which dissolves easily in water with a violet color. It gives a reddish violet color to alcohol, though it is only slightly soluble in it.

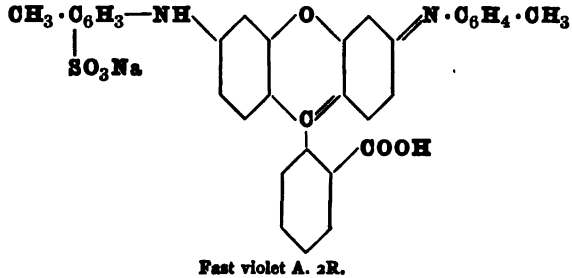
Hydrochloric acid causes blue flocks to separate, while sodium hydroxide causes no change save to turn the solution a cherry red color. The solution in strong sulphuric acid is first a reddish yellow, then on adding water violet, and finally blue flocks separate.

Silk and wool are dyed a violet which resists fading and equalizes well. Upon silk weighted with tin salts it is a very fast shade.

Fast Violet A. 2R. (1888), (Violamine R.), is almost identical with the last named dye, for it differs only in containing two

methyl groups in addition to fast violet B. These are implanted in the molecule by employing orthotoluidine in place of aniline to react with fluoresceine chloride. The process is the same as for the above dye and the final step is treating with sulphuric acid to form the sulpho acid. The sodium salt of this sulpho acid is the dye.

The influence of the two additional methyl groups is to give a redder shade of violet; their position may be seen in the formula.



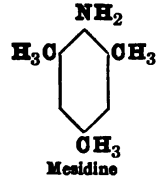
Fast violet A. 2R.

Fast Violet A. 2R. is a violet red powder which easily dissolved in water with a violet red color. It is soluble in alcohol with the same color.

Hydrochloric acid causes bluish red flocks to separate, but sodium hydroxide has no effect. The solution in strong sulphuric acid is yellowish red; on adding water, bluish red followed by a separation of bluish red flocks.

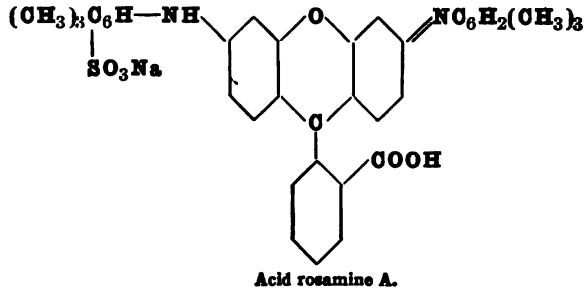
Silk and wool are dyed a reddish violet. The dye equalizes well and is fast to light and alkalis. It is not sensitive to acids nor to washing.

Acid Rosamine A. (1891?), (**Violamine G.**), is formed by the action of mesidine upon floureseine chloride. Mesidine is a trimethylaniline whose methyl groups are arranged as shown below:



Mesidine

Two molecules of mesidine react with fluoresceine chloride and when the resulting product is sulphonated, the constitution is:



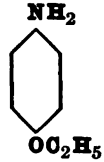
Acid rosamine A.

Acid rosamine is a bright red powder whose aqueous solution is yellowish red. Red flocks separate on adding hydrochloric acid. Sodium hydroxide only turns it yellower.

It dissolves in strong sulphuric acid with a brown color which changes to reddish brown as water is added; then red flocks separate.

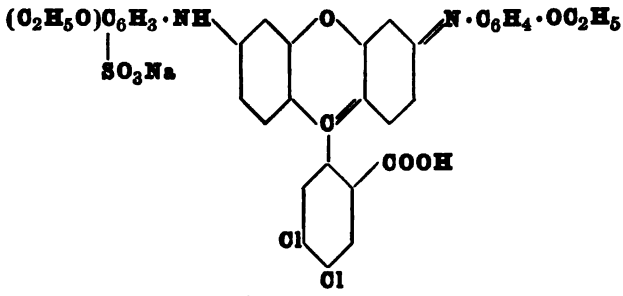
Silk and wool are dyed a lively rose color which does not easily fade.

Fast Acid Blue R. (1889), (Violamine 3B.), is a more complex dye than the last described in two particulars. The fluoresceine chloride has two chlorine atoms in the phthalic acid ring and it is therefore a dichlor fluoresceine chloride. Upon this paraphenetidine is allowed to react and its constitution is shown below as an ethoxyaniline.



Paraphenetidine

When two molecules of this substance have reacted with dichlor fluoresceine and the product sulphonated, the dye then is formed by neutralization as a sodium salt:



Fast acid blue R.

Fast acid blue R. is a dark bluish violet powder. In water it is easily soluble with a dark blue color. In alcohol it is slightly soluble with the same shade.

Blue flocks separate by adding hydrochloric acid. Sodium hydroxide changes it to violet which on heating turns red. In strong sulphuric acid it is first red, which an addition of water turns reddish violet with a separation of blue flocks.

The dye equalizes well and silk and wool are dyed a fast blue shade.

CHAPTER XI

THE INDAMINES, INDOPHENOLS, THIAZINES, OXAZINES

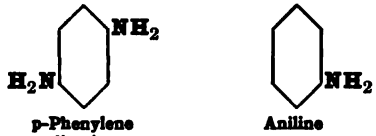
The Indamines

The indamines are among the oldest dyestuffs known, for they were formed in the oxidation experiments which were carried out upon aniline by Runge and Perkins more than half a century ago.

They are all blue to green in color and would have been available as dyes were it not for their sensitiveness to the action of acids. Indeed, if an excess of acid be present, they are decomposed directly into a quinone and amines.

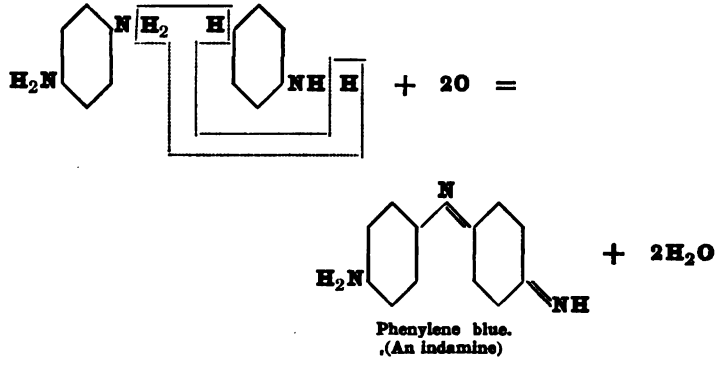
Although their instability prevents their use as dyes, they yet possess a theoretical and practical interest as intermediate products in the manufacture of the safranines.

The simplest materials which may be employed for forming an indamine are *p*-phenylenediamine and aniline and the resulting product is phenylene blue.



p-Phenylene diamine — Aniline

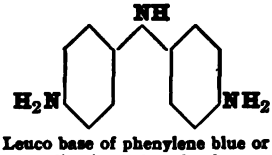
Oxidizing agents remove hydrogen atoms from one amino group of the *p*-phenylenediamine and from both the amino group and the benzene ring of the aniline. A union of the two residues is thus effected while the hydrogen is separated as water. The parts of the two molecules involved forming the combination are shown in the equation:



Phenylene blue.
(An indamine)

To produce this blue dye, equal molecular quantities of the two substances are oxidized by potassium bichromate in a cold neutral aqueous solution.

By reduction the blue color of the dye fades into the white of the leuco compound and this change is effected by the taking up of a hydrogen atom by each of the nitrogen atoms exhibiting a double bond. This leuco compound is identical with *p*-diaminodiphenylamine.

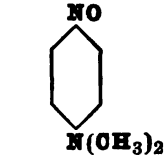


Leuco base of phenylene blue or
p-diaminodiphenylamine

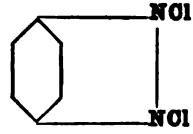
By oxidation these two hydrogens are removed and the phenylene blue is restored.

Phenylene blue is too sensitive to acids for employment as a dye. It is introduced to show the linking together of two benzene rings by a nitrogen atom, the first step toward the formation of the safranines.

In the above reaction, the *p*-phenylenediamine may be replaced by such substances as yield paradiamines upon reduction, nitrosodimethylaniline and dichloroquinoneimide are examples.

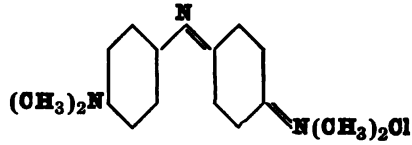


Nitrosodimethyl-aniline



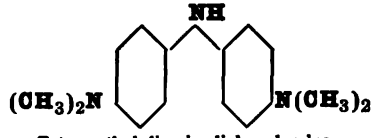
Dichloroquinone-imide

Bindschedler's Green. If in place of *p*-phenylenediamine, dimethylparaphenylenediamine and in place of aniline, dimethylaniline are used and the mixture subjected to oxidation, a green dye known as Bindschedler's green results instead of phenylene blue. In other words, the fixation of four methyl groups upon the amino and imido nitrogens of the phenylene blue changes the color to green. These requisite methyl groups are brought into the reaction by the employment of initial substances that are already enriched by methyl groups which the course of the reaction leaves undisturbed.



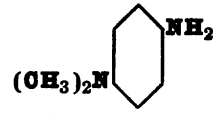
Bindschedler's green.
(Dimethyl-p-phenylenediamine + dimethylaniline.)

Bindschedler's green dissolves in water with a beautiful green color. Alkalies change the color to a beautiful blue. If it is reduced, hydrogen is taken up in the same manner, as by phenylene blue, and tetramethyl diaminodiphenylamine is formed; the green color fades away with the formation of this leuco compound.



Tetramethyl-diaminodiphenylamine.
Leuco-Bindschedler's green

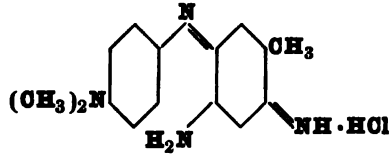
Witt's Toluylene Blue. Oxidation of a mixture of dimethyl-*p*-phenylenediamine and *m*-toluylenediamine produces a reaction analogous to that in forming the foregoing dyestuffs. Toluylene blue is thus formed.



Dimethyl-p-phenylenediamine

m-Toluylenediamine

The dyestuff has the following composition:

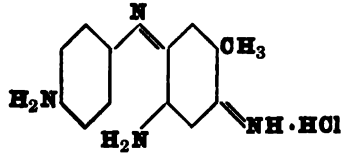


Toluylene blue

Toluylene blue is distinguished from the other indamines described above by its greater stability. The salts formed with one molecule of acid are blue; those formed with two molecules of acid are colorless. Reduction converts it into leuco compound triaminotolylphenylamine.

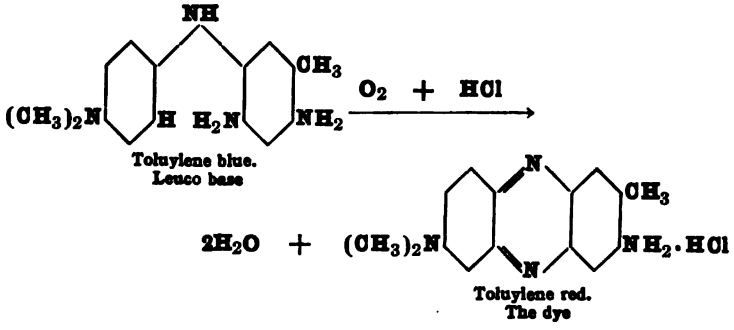
Witt's toluylene blue has attained considerable theoretical importance because of its transformation on heating with water into a eurhodine called neutral red. The character of this change will be shown under the eurhodines.

In a similar manner an indamine is formed by the oxidation of *p*-phenylenediamine and *m*-toluylenediamine. The resulting compound is simpler than Witt's toluylene blue by the two methyl groups which in that dye were substituted for the hydrogen of the amino group.



Simpler toluylene blue

This indamine is of interest since by simply boiling with water it is converted into the eurhodine, toluylene red. (See this.)



The Indophenols

The indophenols have both in structure and in the substances employed for their production a close resemblance to the indamines. Indeed it is possible to convert an indamine by the action of potassium hydroxide into an indophenol.

As *p*-phenylenediamine is the starting point in the formation of the indamines so it is likewise in the manufacture of the indophenols.

The simplest indophenol is produced by the simultaneous oxidation of paraphenylenediamine and phenol. If an amine, e.g., if aniline had been used in place of phenol, an indamine would have been formed.

$$\underset{\text{Paraphenylene-diamine}}{H_2NC_6H_4NH_2} + \underset{\text{Phenol}}{C_6H_5OH} + O_2 =$$

$$HN{=}C_6H_4{=}N{-}C_6H_4{-}OH + 2H_2O$$

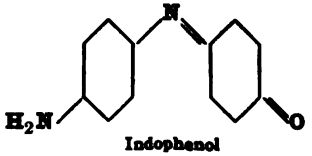
Indophenol

According to its properties the structure of the indophenol should be written as follows:

$$H_2N{-}C_6H_4{-}N{=}C_6H_4{=}O$$

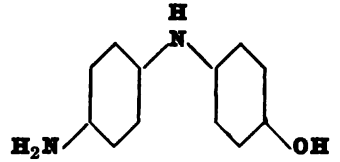
Indophenol

or



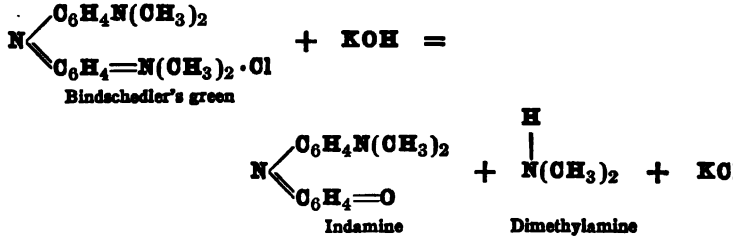
Indophenol

This formula, exhibiting a quinone oxygen, is the more probable from the fact that this substance possesses no acid properties which it would be expected to show if a hydroxyl group were present. This view is further supported by the fact that the leuco indophenol, formed by the action of two hydrogen atoms breaking the double bonds, does exhibit weak acid properties. This shows the presence of a hydroxyl as shown in the formula:



Leuco indophenol or Indophenol white

An instance of the direct transformation of an indamine into an indophenol is shown by the action of potassium hydroxid upon Bindschedler's green. Dimethylamine is eliminated at the same time.



Bindschedler's green

Indamine Dimethylamine

Thus the close relation between the indophenols and indamines is made at once apparent.

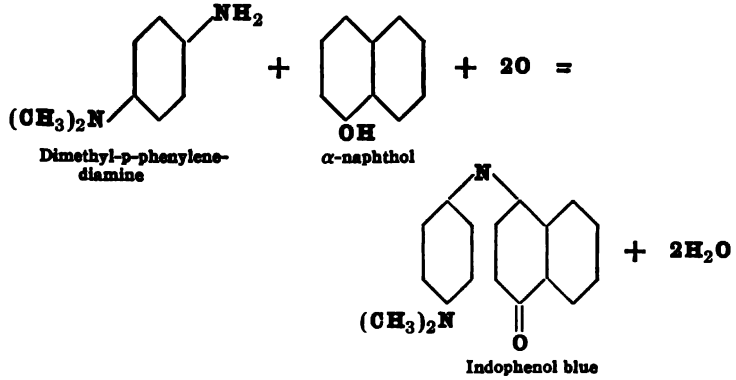
The leuco indophenols exhibit in a pronounced degree the character of phenols. They dissolve in solutions of the caustic alkalies. They are, however, easily oxidized in this alkaline solution by the action of the air and at once changed into the indophenols, which, being insoluble in alkalies, separate from the solution. In acid solutions the leuco indophenols are not thus affected by atmospheric oxygen.

Upon the solubility of the leuco indophenol in alkaline solution and its easy atmospheric oxidation depends its use in dyeing.

Indophenol itself apparently from its chemically indifferent character shows no affinity for the textile fibers. This difficulty is overcome in practice by a process exactly like that for indigo dyeing. The fibers are immersed in an alkaline solution of leuco indophenol. This colorless substance does have an affinity for the fibers and they become in consequence thoroughly impregnated with it. Exposure to the air then develops the color by oxidation. A bath of potassium bichromate may also be used for the development of the color.

Direct dyeing of its fibers has been accomplished by impregnating them with an amine and a phenol and then passing slowly through a bath of potassium bichromate or bleaching powder, which develops the color at once.

Indophenol Blue. The only indophenol of technical value is the one produced by the combination dimethylparaphenylenediamine and α-naphthol.



The commercial dye is a dark brown powder or a dark blue paste with shining bronze lustre. It does not dissolve in water; alcohol dissolves it to a blue solution. Hydrochloric acid turns the blue alcoholic solution to a reddish-brown. Sodium hydroxide has no effect upon the same solution.

It is decolorized by stannous chloride. Concentrated sulphuric acid yields a yellowish-brown solution from which the addition of water causes the separation of brown precipitate.

It is employed for producing indophenol white, in which form the application is made to the technical fibres.

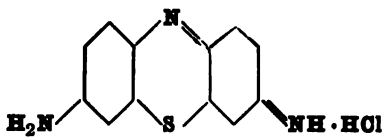
Indophenol blue is sensitive to the actions of acids and it is decomposed by them in the same way as the indamines. In the pressure of an excess of acid, indophenol blue is separated in α-naphthoquinone and dimethyl-*p*-phenylenediamine. This sensitiveness to acids has retarded the use of indophenol blue in printing and dyeing, for it is otherwise particularly adapted on account of its indigo color, the fastness to washing and its cheapness, to become a formidable rival of indigo. Furthermore it is affected by the action of steam.

A new sphere of usefulness has latterly appeared for the indophenols in the production of the sulphur dyes.

The Thiazines

The name for this class of dyes is derived from the Greek (*θεῖον*, sulphur) and French (*azote, nitrogen*). These dyes resemble the indamines and indophenols in their structure. The entrance of an atom of sulphur into the molecule, for instance, of an indamine confers upon these new dyes their characteristic properties.

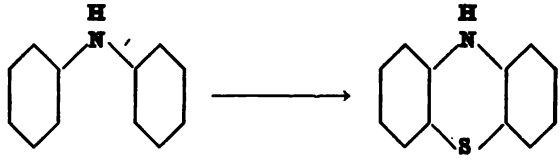
The most marked advantage accruing from the acquisition of this sulphur atom is the diminished sensitiveness to the action of acids. This sulphur atom takes up a certain central place in the dye molecule which is in the ortho position to the nitrogen atom in diphenylamine. It unites with a carbon atom in each benzene ring and this while binding the two rings together it helps to form a new central ring made up as may be seen from the following formula of four carbon atoms, one nitrogen, and one sulphur atom.



Lauth's violet

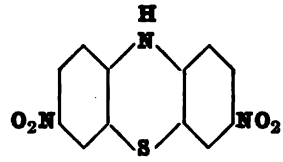
In 1876 Lauth discovered the first dye of this class and it received the name of Lauth's violet. If paraphenylenediamine in a solution containing hydrogen sulphide be oxidized by ferric chloride, Lauth's violet is produced. That the constitution of this dye as indicated above is correct was proved by Bernthsen in the following brilliant manner.

By the action of sulphur upon diphenylamine, a thiodiphenylamine was formed.



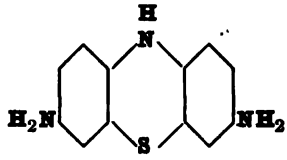
Diphenylamine — Thiodiphenylamine

Upon nitrating this product two nitro groups become fixed in positions which are para to the imido nitrogen, thus forming paradinitrothiodiphenylamine.



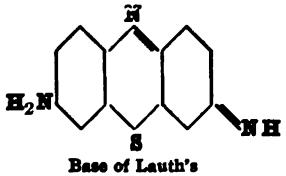
Paradinitrothiodiphenylamine

By reduction the two nitro groups are converted into amino groups and diparaaminothiodiphenylamine is the result.

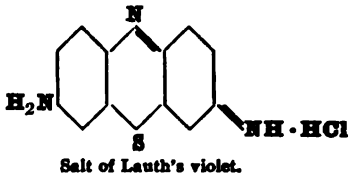


Paradiaminothiodiphenylamine

This compound is in every way the same as the leuco base of Lauth's violet and by oxidation it is converted directly into that dyestuff.



Base of Lauth's violet

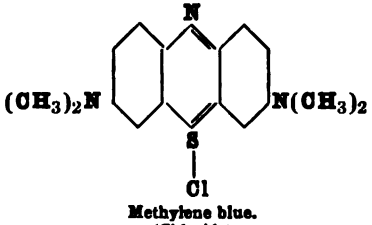


Salt of Lauth's violet. The dye

Lauth's violet is a beautiful dye, but on account of the poor yield—20 per cent of the theoretical—and the consequent high cost, it never met with extensive practical application. It is now superseded by one of the most important dyes, called methylene blue.

Methylene Blue (1876). By replacing the four amino hydrogens of Lauth's violet with methyl groups, methylene blue would be formed. It is not prepared in this manner; but it is of interest to note that the entrance of four methyl groups induces a change from violet to blue, and further that the more complex product is easier of manufacture and of more extensive application.

This dyestuff was first discovered by Caro, who prepared it by the oxidation of dimethylparaphenylenediamine in a solution containing hydrogen sulphide. Its constitutional formula allows of easy comparison with Lauth's violet given above.



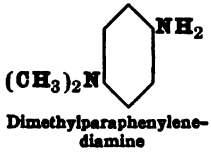
Methylene blue. (Chloride)

For its technical preparation nitrosodimethylamiline $ONC_6H_4N(CH_3)_2$ was reduced with either hydrogen sulphide or zinc dust and the dimethylparaphenylenediamine so produced was oxidized with ferric chloride in the presence of hydrogen sulphide. Zinc chloride was added and the com-

bination which this made with the dye was the commercial methylene blue. Addition of common salt separated it from the solution.

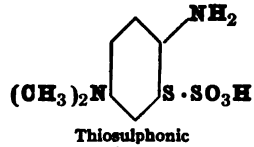
During its formation, two molecules of dimethylparaphenylenediamine are brought together; one nitrogen is eliminated to allow the combination to take place. This nitrogen escapes in the form of ammonia gas.

At present an improved process which employs sodium thiosulphate has almost completely superseded the other methods. In carrying out this method, one molecule of dimethylparaphenylenediamine and one molecule of dimethylaniline are oxidized in the presence of zinc chloride. The reactions which take place and the intermediate products formed may be represented as follows:



Dimethylparaphenylene-diamine

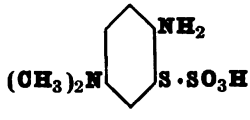
$$+ \; H_2S_2O_3 + O =$$



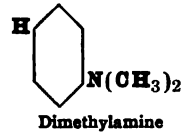
Thiosulphonic acid of the same

$$+ \; H_2O$$

With this product, the dimethylaniline enters into reaction.

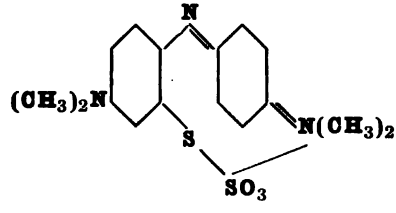


$$+$$



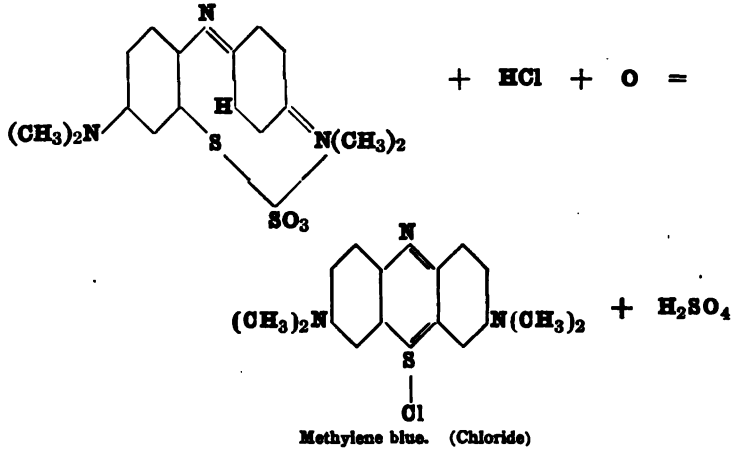
Dimethylamine

$$+ \; 2O =$$



$$+ \; 2H_2O$$

By further oxidation of this the central ring is closed and by combining with the hydrochloric acid, the methylene blue is formed.



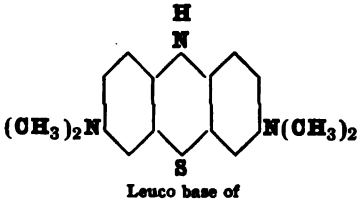
Methylene blue. (Chloride)

The thiosulphate process for the manufacture of this dye has the advantage of requiring only one-half as much dimethylparaphenylenediamine as the other processes: because of the possibility of employing dimethylaniline—a more easily accessible and cheaper substance.

Moreover by this method the yield is greater and the product also of greater purity.

The free base is separated with difficulty from its salts, but this may be obtained by the action of moist silver oxide upon the hydrochloride when a hydroxyl probably replaces the chlorine.

By reduction it takes up two hydrogens and passes easily into its leuco-base, tetramethyldiaminothiodiphenylamine.

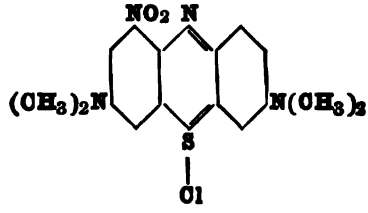


Leuco base of methylene blue

This base appears in the form of colorless leaflets which cannot endure exposure to the air without being rapidly oxidized again to the blue dye.

Methylene blue is the most important of all the blue basic coloring matters. It is especially fast to light and extensive application is found for it in cotton printing and dyeing, in which processes it is by the use of tannic acid fixed upon the fibre in the form of a tannin salt or lake. It is especially adapted for the production of sky blue tints and in accordance with its character it shows little affinity for wool, and it shows when dyed upon wool an extreme sensitiveness to light. It is also but poorly adapted for dyeing silk. For the production of certain shades methylene blue is toned with methyl violet, malachite green, or other basic colors. The methylene blue, freed from the zinc chloride contained in the commercial dyestuff, is employed in medicine because of its valuable antiseptic qualities.

Methylene Green (1886). If a single nitro group is implanted in the molecule of methylene blue it is changed into the dye methylene green. To produce this change it is only necessary to dissolve the blue dye in concentrated sulphuric acid and treat it with one molecule of nitric acid. In one of the benzene rings a single nitro group becomes fixed upon the carbon atom which is next to the nitrogen as shown in its formula:



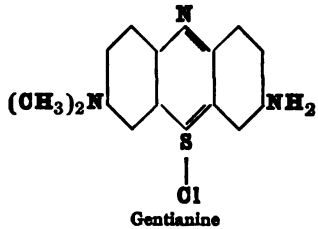
Methylene green. (Chloride)

It is therefore a mononitromethylene blue. The commercial product is a dark brown powder which easily dissolves in water with a greenish-blue color. In alcohol it is but sparingly soluble. Hydrochloric acid does not affect it, sodium hydroxide

causes a separation of violet-colored flocks. In concentrated hydrochloric acid it dissolves with a dark green color and this on dilution changes to blue.

Gentianine (1886). This dye stands in relation to its constitution half way between Lauth's violet, of slight commercial value, and methylene blue, which is of great industrial importance. In Lauth's violet the four amino hydrogens remained unsubstituted, in methylene blue all four hydrogens were substituted by methyl groups, but in Gentianine G. only two of these hydrogens in one amino group have been replaced. The effect has been to produce a dye neither blue nor violet, but a bluish-violet.

In its preparation paraphenylenediamine and paramino-dimethylaniline are oxidized, in a solution containing hydrogen sulphide, by the addition of ferric chloride. Its formula is:



Gentianine

It appears in commerce in the form of a zinc chloride double salt, which is a reddish-brown powder. Water dissolves it easily, forming a bluish-violet solution; it dissolves less easily in alcohol. Hydrochloric acid turns the solution greener. Sodium hydroxide changes the color to violet and then causes a dirty violet precipitate. Concentrated sulphuric acid yields a yellowish-green solution which the addition of water turns first blue and then blue-violet.

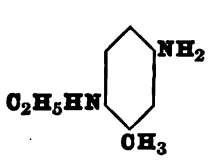
The leuco-base is easily produced by reducing agents and oxidizing agents quickly restore the color of the dye.

It is employed to dye cotton which has been mordanted with tannin a bluish-violet.

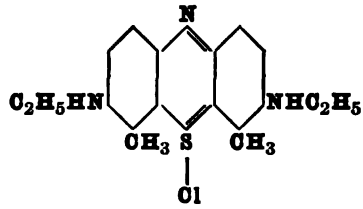
New Methylene Blue N. (1891). This dye produces redder and fuller shades than methylene blue, and it owes these properties

to the methyl and ethyl groups with which methylene blue may be regarded as enriched. Its preparation may be carried out by the sodium thiosulphate process described under methylene blue.

The oxidation of two molecules of monoethylorthotoluylenediamine produces the dye.



Monoethyltoluylenediamine



New methylene blue N. (Chloride)

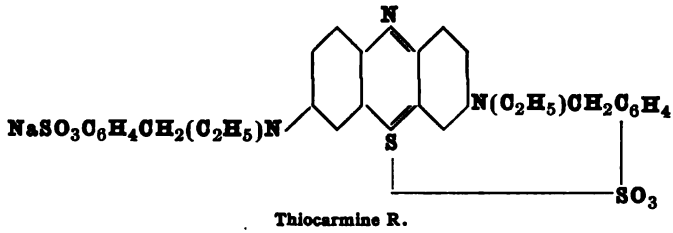
It is a brown crystalline powder of metallic lustre which dissolves easily in water with a blue color and in alcohol with a greenish-blue. Addition of hydrochloric acid produces a pure blue, while sodium hydroxide causes the separation of a brown precipitate.

A yellowish-green solution is formed with concentrated sulphuric acid, but this is changed to a pure blue by adding water.

The color when once reduced to its leuco-base by zinc dust is at once restored by exposure to the air.

Thiocarmine R. (1890). The basic thiazines thus far described are not suitable for dyeing wool. By the process of sulphonation the basic character is neutralized and a predominating acid character is developed. Thiocarmine is such a sulphonated thiazine which is used for wool dyeing. It may be regarded as a methylene blue which has been enriched with both benzyl groups ($C_6H_5CH_2$) and sulphonic acid groups.

For its preparation aminoethylbenzylanilinesulpho acid is employed as a starting point and it is subjected to oxidation by chromic acid in the presence of sodium thiosulphate. By this process a thiosulphonic acid is formed, which is then condensed with ethylbenzylanilinesulphonic acid when by the further action of heat the thiocarmine results.



Thiocarmine R.

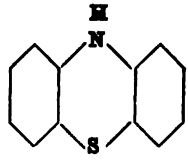
Thiocarmine R. comes into the trade in the form of an indigo blue powder or paste. Hydrochloric acid does not affect it nor does sodium hydroxide in a cold solution, but on heating a change to violet takes place. The solution in strong sulphuric acid is green, but on dilution it becomes blue.

When it is reduced by zinc dust and then exposed to the air, the color returns.

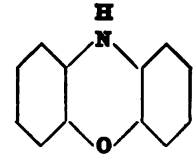
It is distinguished by its power of equalization, that is, the dye attaches itself to the fibre in a uniform manner, and it is recommended as a substitute for indigo carmine, although it has less resistance to the action of light. To acids, alkalies, and the process of milling, thiocarmine is reasonably fast.

The Oxazines

From the thiazines, the transition to the oxazines is easily made so far as the conception is concerned. If oxygen is substituted for the atom of sulphur in the centre ring of the thiazines, then the thiazines result. The latter may all be regarded as derivatives of phenoxazine; for this appears as the central nucleus of this whole class of dyes. At the same time, it may be seen how the oxazines and thiazines differ by comparing the following formulas:

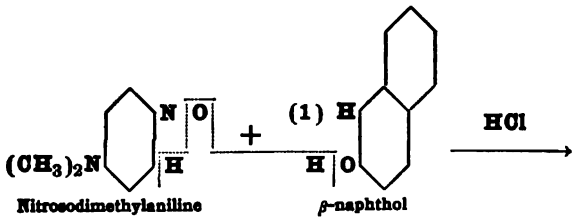


Nucleus of the thiazines or thiodiphenlyamine

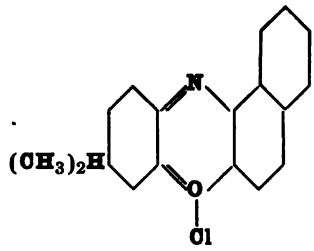


Nucleus of the oxazines or phenoxazine

Meldola's Blue (1879). When nitrosodimethylaniline and β-naphthol are brought together in solution in glacial acetic acid, a condensation occurs and a blue dye is formed. This process for producing a blue dye was discovered in 1879 by Meldola and hence the product bears the name of Meldola's blue. The character of the reaction is shown below.



Nitrosodimethylaniline β-naphthol



Meldola's blue. (Chloride)

For convenience in writing the formula, the naphthol molecule is somewhat distorted from its usual form. The one oxygen atom which is eliminated in the form of water is not sufficient to remove all of the hydrogen necessary to enable the condensation to take place. This extra hydrogen No. 1, in the formula above is oxidized by an excess of nitrosodimethylaniline and this is in turn by this very operation reduced to dimethyl-*p*-phenylenediamine. This latter substance is always found in the mother liquor of the manufacture.

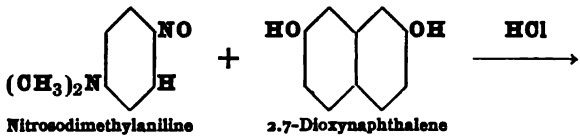
Latterly an improvement has been made in the preparation of this dye by employing alcohol as the solvent for the reaction in place of glacial acetic acid.

Meldola's blue is a dark violet-colored powder with a bronze lustre. The mucous membranes are violently attacked by the dust which arises in shaking or pouring the powdered dyestuff.

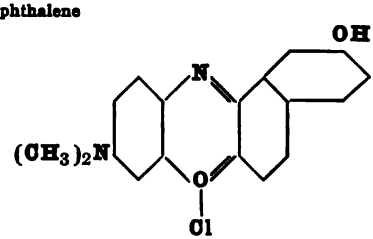
It dissolves easily in water with a bluish-violet color. Hydrochloric acid causes the violet solution to turn blue. Sodium hydroxide causes a brown precipitate. A blackish-green solution is effected in strong sulphuric acid, which changes to blue on diluting with water.

Cotton which is mordanted with tannin and tartar emetic is dyed blue. It is also suitable for dyeing silk and wool. The color resists very well the action of light, acids, and soap: but it is not so stable against alkalies. It is employed as a substitute for indigo.

Muscarine (1885). This is a blue dye produced by condensation of the two components, nitrosodimethylaniline and 2.7 dioxynaphthalene acting upon one another.



Nitrosodimethylaniline 2.7-Dioxynaphthalene



Muscarine. (Chloride)

Muscarine forms a brownish-violet powder which dissolves with difficulty in cold but easily in hot water, with a bluish-violet color. Boiling the aqueous solution with zinc dust decolorizes it by converting it into the leuco compound. On exposure to the air, oxidation causes the bluish color to return.

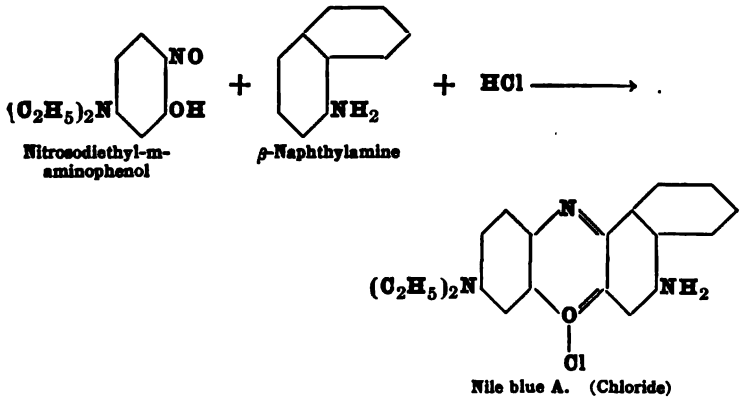
Hydrochloric acid produces a violet precipitate, while sodium hydroxide dissolves the dye to a yellowish-brown solution. Strong sulphuric acid forms a bluish-green solution that by gradual dilution with water changes first to blue, then to violet: finally a violet precipitate fails.

Cotton which has been mordanted with tannin and tartar emetic is dyed a moderately fast blue. It is also employed in cotton printing.

By comparing muscarine with Meldola's blue, it will be seen that the only difference is a single hydroxyl group which the former possesses in position 7. This has the effect upon its chemical properties of giving a blue shade and a livelier tone.

A dyestuff has been prepared analogous to muscarine, which has the hydroxyl in position 6 instead of 7, and this change of position changes the color produced upon mordanted cotton from blue to green.

Nile Blue A. (1888), has the familiar nucleus of an oxazine. It is formed by the condensation of nitrosodiethyl-*m*-aminophenol with *α*-naphthylamine. The structure of these substances is seen below.



This reaction is carried on in the presence of hydrochloric acid and the salt which is the dye is at once developed with the constitution shown in the formula above.

Nile blue A is employed with a tannin mordant, and is noted for the purity of its effects.

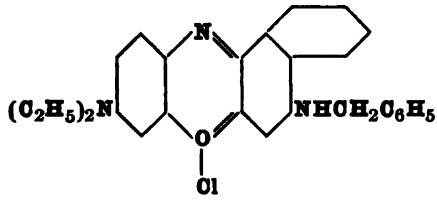
In commerce it is a green crystalline powder possessing a bronze lustre which is soluble with difficulty in cold water, but easily soluble in warm water, to which it imparts a blue color. Alcohol will dissolve it with the same color.

If hydrochloric acid is added to the warm aqueous solution, the hydrochloride is precipitated in the form of fine needles, which are green in reflected light, but violet in transmitted light. Sodium hydroxide produces a red precipitate which will dissolve in ether with a brownish-orange color with a dark green fluoresence. It dissolves in strong sulphuric acid with a brown color that changes with addition of water first green and then blue.

Cotton is mordanted with tannin and tartar emetic, and then dyed blue while it is not found to be suitable for wool.

Reducing agents transform it into the leuco base which on exposure to the air rapidly turns blue again.

Nile Blue 2B. (1891), is a dye closely resembling Nile blue A, described above. The color produced by it upon mordanted cotton is a greenish-blue instead of a pure blue. This effect corresponds to a change in the composition and this depends upon the use of benzylnaphthylamine in place of the simpler naphthylamine used for the Nile blue A. Except for the benzyl residue, it has the same constitution as that dyestuff.



Nile blue 2B.
(Chloride)

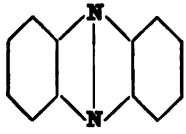
This dye appears as a crystalline powder of a greenish lustre. Cold water dissolves it with difficulty; but in either hot water or alcohol it easily dissolves with a greenish-blue color. The addition of a little hydrochloric acid induces the separation of reddish-violet flocks, while a large amount forms a brownish-yellow solution. A brownish-red precipitate follows the addition of sodium hydroxide. The brownish-red solution which it forms with strong sulphuric acid lets fall a violet precipitate when water is added.

CHAPTER XII

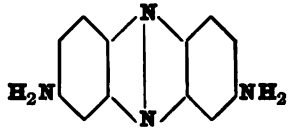
THE EURHODINES AND SAFRANINES

The Eurhodines

The eurhodines are the simplest of the azine dyes and consist of two benzene rings joined by the azine group further with amino groups symmetrically attached to the rings. They are in consequence diaminophenazines.



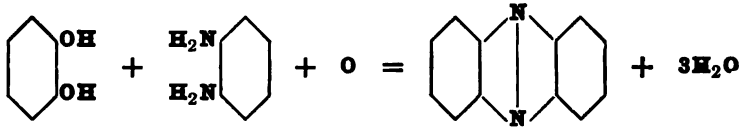
Phenazine



Diaminophenazine.
Nucleus of eurhodines

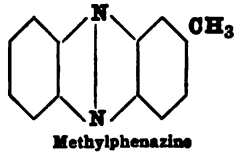
The proof of the structure of the eurhodines may be understood from the following reactions:

Phenazine was produced by condensing pyrocatechol with *o*-phenylenediamine, three molecules of water being eliminated.



Pyrocatechol | *o*-Phenylene-diamine | Phenazine

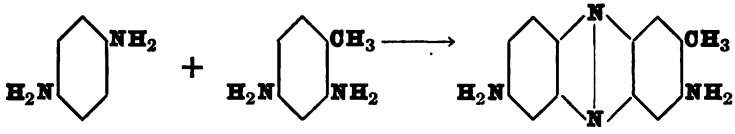
If *o*-toluylenediamine is condensed with pyrocatechol we obtain similarly methylphenazine.



Methylphenazine

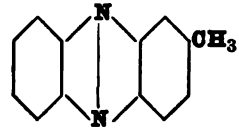
Now methylphenazine can be prepared and was prepared in another way, the study of which reveals clearly the connection of the eurhodines to phenazine.

By a process of oxidation and subsequent heating, the two compounds *p*-phenylenediamine and *o*-toluylene are condensed to simple toluyene red.



p-Phenylene-diamine | o-Toluylene-diamine | Toluylene red. Color base

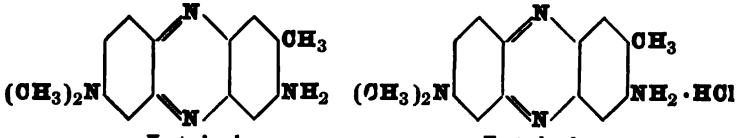
When this toluylene red is diazotized, a tetrazo compound is formed. If this tetrazo product is boiled with alcohol, two amino groups are eliminated and methylphenazine results.



Methylphenazine

From these reactions and products, it is concluded that the simple tolulyene red is a diaminomethylphenazine, and that it has the constitution shown above.

Neutral Red (1879). The eurhodine known as neutral red is formed similar to that for toluylene red given above. The two substances brought together for this purpose are dimethyl-*p*-phenylenediamine and *m*-toluylenediamine. By oxidation, these substances unite and pass through the interesting phase of first forming a blue substance called toluylene blue. The product is then boiled, whereby it is transformed into neutral red.



Neutral red. The base | Neutral red. The dye

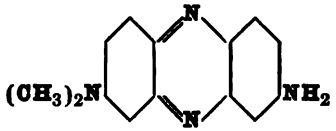
Here we have substances analogous to those condensed to produce toluylene red, which was converted into methyphenazine and thus proved a diamino derivative of phenazine: the neutral red employs a dimethyl-*p*-phenylenediamine in place of the simpler *p*-phenylenediamine, the two methyl groups not affecting the condensation whereby the dye is formed. Neutral red is a dark blackish-green powder, which communicates a carmine red color to its aqueous solution, while it dissolves in alcohol with a magenta red shade that exhibits a slight brownish-red fluorescence.

The first effect of hydrochloric acid is to turn it blue, producing a pure blue when an excess has been added. A yellowish-brown precipitate falls on adding sodium hydroxide, and this precipitate dissolves in alcohol or ether, giving strongly fluorescent solutions.

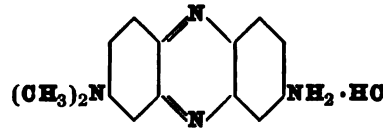
Dissolved in strong sulphuric acid, the color is green; this changes on diluting, first to blue and then to magenta red.

From a neutral bath, cotton mordanted with tannin is dyed a bluish-red.

Neutral Violet (1879). This dye differs from neutral red only in having a methyl group less; the removal of this methyl group from its position in the benzene ring works a decided change in the color of the dye, turning it from red to violet.



Neutral violet.
The base



Neutral violet.
The dye

Neutral violet is a greenish-black powder which, inhaled in the form of dust, violently attacks the mucous membranes of the nose and throat, causing sneezing.

Water easily dissolves it, giving a violet-red solution. Only a slight change is caused by hydrochloric acid until an excess has been added, when the color becomes blue. A brown precipitate falls on adding sodium hydroxide. A green solution is formed with strong sulphuric acid; but this changes to

blue and then to violet as water is slowly added. Cotton mordanted with tannin is dyed a reddish-violet.

The Safranines

The safranines are among the oldest of the coal-tar dyes. Indeed, mauve, the very first dye prepared by Perkin in 1856, has been shown after long-continued research to be a true safranine. Few dyes have presented more difficulties in determining their composition and structure or have enlisted such frequently repeated attempts of many chemists to attain formulas which should give rational explanation of the syntheses, properties, and reactions of these dyes.

The most striking property of these dyes is their strongly marked basic character, which in many respects claims kinship with the ammonium bases; further, among other peculiarities, they have a characteristic bitter taste.

The safranines, as members of the azines, contain a double nitrogen group , and their strongly basic nature may be ascribed to this group. Two amino groups are also present. The hydrogen atoms of these amino groups may be replaced by acetyl groups. Even then the nature of the molecule as a whole, though acid radicals are present in the amino groups, remains basic, lending support to the view that the azine group is responsible for their behavior as strong bases.

The safranines are capable of forming three classes of salts with acids, according to the strength of the acids employed. The monacid salt is the most stable and is not decomposed by water, while the diacid and triacid salts cannot exist in the presence of much water.

The three salts exhibit very different colors. The stable monacid salt is red; the diacid salt requiring a weak acid solution to keep it from decomposing is blue; the triacid salt which can exist only in the presence of strong sulphuric acid or very strong hydrochloric acid is green. In view of these facts, it is easy to see how a solution of the dye safranine

itself in strong sulphuric acid, which at first is green, will pass through a blue phase to the final and stable red color as the gradual addition of more and more water decomposes in succession triacid, then the blue diacid salt, leaving the red monacid salt able to maintain its stability in an aqueous solution.

By reduction, the safranines are converted into leuco-compounds which possess a double character according to the circumstances; being quite stable in acid solution, but, if produced in an alkaline solution, they become oxidized almost immediately back to their original color by the oxygen of the air.

If stannous chloride and hydrochloric acid are used for the reduction, it is found that one molecule of the chloride is able to reduce one molecule of safranine to its leuco-base. Hence it follows that only two atoms of hydrogen are added to the molecule during the conversion.

Safranines are formed by many methods, among which are the following:

1. By heating indamines with primary monamines, with partial reduction of the latter.

2. By the simultaneous oxidation of *p*-diaminodiphenylamine and its analogues with primary aromatic amines.

3. By a similar oxidation of *p*-diamines and two molecules of primary bases.

4. Finally, by oxidation of *m*-aminodiphenylamine or its analogues and *p*-diamines.

The safranines are also formed from the reaction of amines upon aminoazo compounds.

Technical Preparation. Their preparation from these latter compounds of course necessitates their reduction, which splits them into *p*-diamines and monamines; for the azo group is not present in the safranines.

In the manufacture almost exclusive use is made of that process wherein one molecule of a *p*-diamine and two molecules of a monamine are united by means of a simultaneous oxidation of all three units.

The required mixture of these amines is obtained by the

reduction of the aminoazo compounds. Usually there is prepared a mixture of aminoazotoluol and *o*-toluidine by diazotizing *o*-toluidine with sodium nitrite and hydrochloric acid. The product is then reduced and consequently split by zinc dust or iron filings acting upon hydrochloric acid. The result is a mixture of one molecule of *p*-toluylenediamine and two molecules of *o*-toluidine; or in place of the latter one molecule of toluidine and one molecule of aniline. This mixture is neutralized with powdered chalk and then, after the addition of potassium bichromate, kept at a boiling temperature for some time. Weldon mud and oxalic acid may be used for the oxidation process in place of the bichromate.

The first products of these oxidations are indamines; but as boiling continues, the excess of the monamine present, by aid of the oxidation that is going on, enters the reaction and converts this first-formed indamine into a safranine.

Simultaneously violet-colored by-products are formed which on account of their weaker basic properties can be made to form a precipitate by the addition of sodium carbonate or chalk and are thus separated from the safranines, which remain dissolved. Later, from this solution, the addition of salt causes the separation of the safranines themselves.

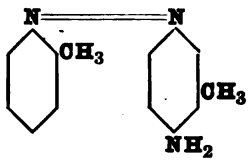
The first safranine is said to have been discovered by Guinin, Marnas and Bounet in Lyons by the oxidation of mauve. It was afterward prepared by heating aniline which contained toluidine with lead nitrite. Another method was to allow the arsenic acid, used for so many years as an oxidizing agent in rosaniline manufacture, to act upon aminoazobenzene. Naturally as intermediate products aminoazo compounds were first formed by the action of lead nitrite.

The dye is now manufactured almost exclusively by the oxidation of one molecule of *p*-toluylenediamine, one molecule of *o*-toluidine, and one molecule of aniline. It is employed principally in dyeing cotton.

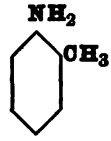
Frequently other yellow dyes, auramine, chrysoidne, and turmeric are used in combination with it to produceithe scarlet tones which are similar to those of Turkey red; but in fastness they are still considerably inferior.

In silk dyeing, safranine is used to produce beautiful shades of rose. Latterly safranine has been diazotized and combined with β-naphthol to produce a blue basic dye which is used in dyeing tannin-mordanted cotton under the name of indoin; this has earned a reputation for great fastness.

Structure of the Safranines. One of the first formulas proposed for safranine made it appear as an azo compound with the characteristic group —N=N— holding together the parts of a complicated molecule. This formula was founded upon the fact that aminoazotoluene and *o*-toluidine when heated together in alcoholic solution produced a safranine.

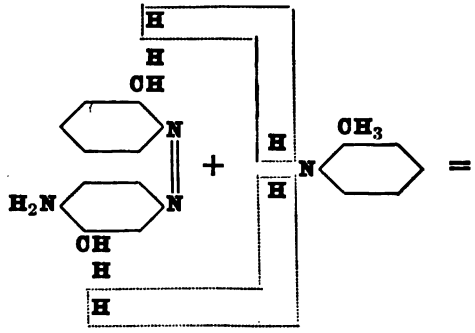


Aminoazotoluene

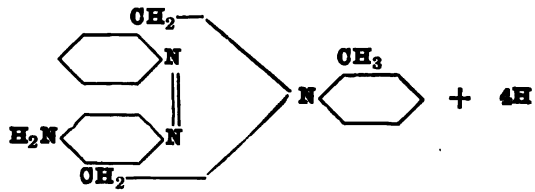


o-Toluidine

The method of their union is seen from the reaction which follows:

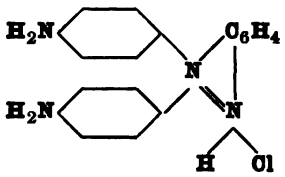


Aminoazotoluene o-Toluidine



Safranine (Witt's formula)

But this formula was shown to be incorrect by a method of preparation where no azo compound was used and where none could be formed during the process. The substances employed were *p*-phenylenediamine and aniline. Oxidation of these two substances yields phenosafranine. It was afterward found that by the simultaneous oxidation of a *p*-diamine and two molecules of a monamine that the safranines themselves could be prepared. This of course shut out of consideration safranines as azo compounds. Nietzki afforded assistance in understanding the safranine formula when he prepared the dye by oxidation of equal molecules of diethyl-*p*-phenylenediamine and aniline. This showed the probable presence in the dye molecule of two monamine radicals with their benzene rings attached. Then by preparing a tetraethylsafranine he supplied further evidence that two amino groups were also present. Leaving out the methyl groups for simplicity, his formula would appear as shown below:



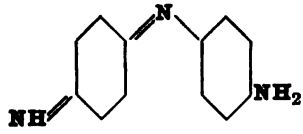
Contrary views, well supported, often came in conflict, and no more interesting and valuable exposition of chemical methods in their progress step by step to the solving the constitutional formula of a dye can be found than that of safranine.

The introduction of the many views and the evidence as it accumulated through a half century would only confuse the student at this point. At present, the structure will be considered in the light of a regular progress from the substances employed until the details of the formula are understood.

Under the indamines, it was stated that these dyes were of little value on account of their sensitiveness to acids. They

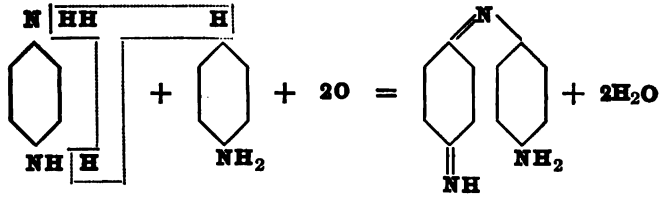
do, however, form a half-way step to the formation of the safranines.

The simplest indamine is a substance containing two benzene rings joined by an amine group and having the other groups affixed in the para positions in these two rings as shown below:



The simplest indamine.
A blue dye

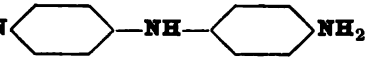
Now this dye is prepared by oxidizing molecular proportions of *p*-phenylenediamine and aniline; we may consider them as forming a union thus:



p-Phenylene-diamine — Aniline — Phenylene blue

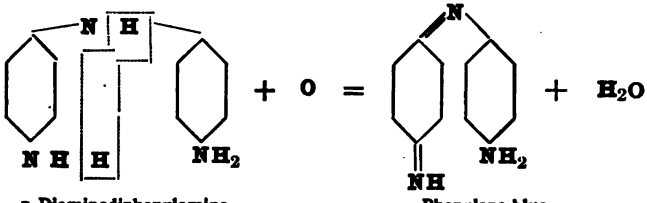
This oxidation and union is brought about by potassium bichromate in neutral solution; but this does not give sufficient reason for writing the formula as just given.

However, it may be clearly established by another method where the two benzene rings are joined by a nitrogen atom and where the amino groups are present, one in each ring in the para position. This method employs *p*-diaminodiphenylamine.

$H_2NC_6H_4NHC_6H_4NH_2$ or 

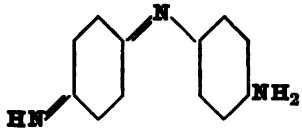
All that is needed to convert this into the indamine known as phenylene blue is the removal of two hydrogen atoms

from the molecule by oxidation in accord with the reaction below:



p-Diaminodiphenylamine Phenylene blue

or



Phenylene blue

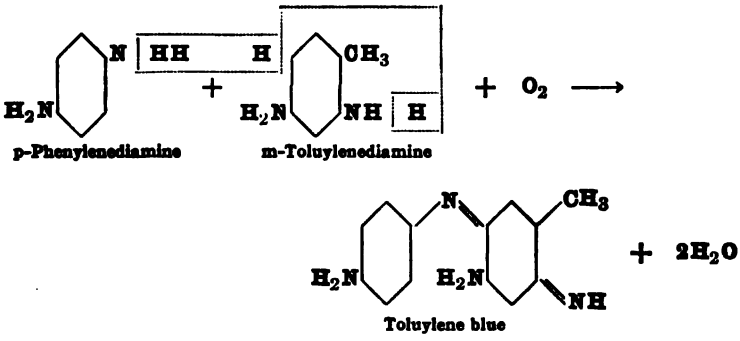
Furthermore by reduction, phenylene blue is converted into a leuco compound which is identical with *p*-diaminodiphenylamine.

It may now be seen that the following facts are clearly established for phenylene blue and also for safranine of which these are a part:

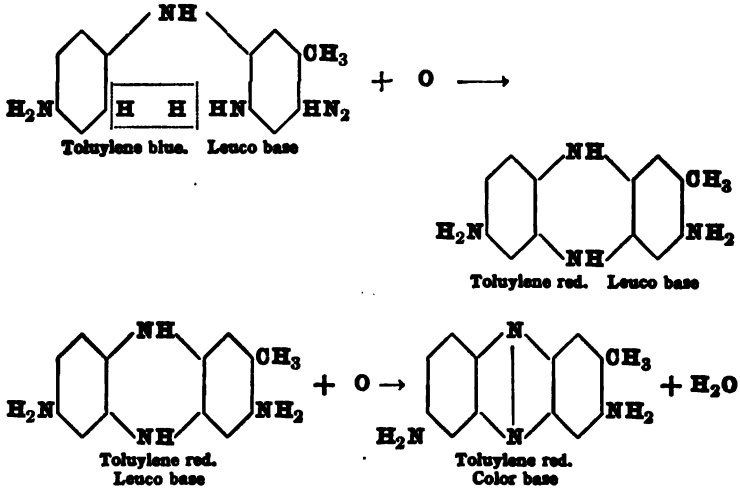
1. Three nitrogen atoms are present in a double benzene molecule.
2. One of these holds the two benzene rings together.
3. Of the remaining two one is present as an amine group in one ring, the other as an amine group in the other ring.
4. Both these amino groups are in the para position to the linking nitrogen.

It is further established that when *p*-phenylenediamine and aniline are oxidized, they will be linked by a nitrogen atom, and the other groups will be in para positions to the linking nitrogen because the product thus obtained is identical with phenylene blue.

Following a similar method of preparation, if we link with *p*-phenylene diamine, in place of aniline, *m*-toluylenediamine, we shall obtain another indamine known as toluylene blue.

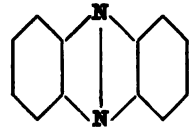


This toluylene blue exhibits the interesting peculiarity of changing into a red dye, on simply boiling with water, known as toluylene red. It is an example of oxidation whereby two hydrogens are removed and a second nitrogen linking takes place within the molecule as follows:



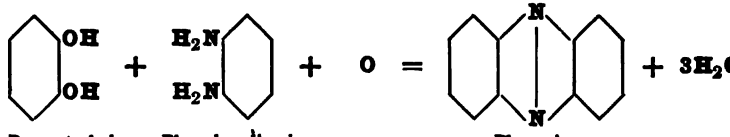
The formation of this new substance by a double linking of a second nitrogen atom is important; for safranine contains a similar one and an understanding of this will help to explain the latter.

But how is it assured that the second nitrogen linking occurs as represented? This double linking of two benzene rings in neighboring or ortho positions forms a substance known as phenazine.



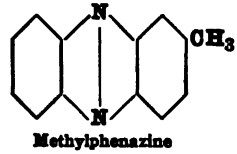
Phenazine

A glance at toluylene red shows that it contains the phenazine as its nucleus. But how may the structure of phenazine be proved to be as represented. It is proved in this manner: Pyrocatechol and *o*-phenylenediamine condense to form phenazine.



Pyrocatechol o-Phenylenediamine Phenazine

Methylphenazine may be prepared in a similar manner by condensing *o*-toluylenediamine and pyrocatechol.

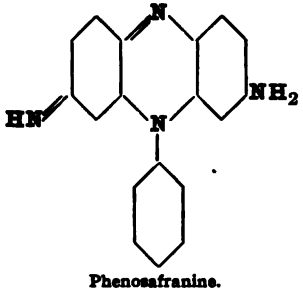


Methylphenazine

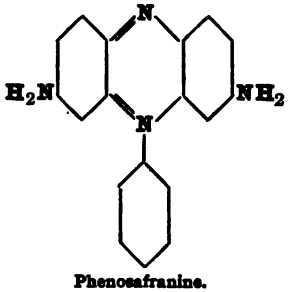
Now a very close relationship exists between toluylene red and methylphenazine which shows conclusively that the phenazine is the nucleus of the red dye. This was proved by Bernthsen and Schweitzer, who, by diazotizing the two amino groups of toluylene red, were able to eliminate them and replace them by hydrogen. The resulting compound was found to be methylphenazine itself.

When *p*-phenylenediamine and two molecules of aniline are oxidized, there is first formed an indamine with its single

nitrogen linking and then by the further action of the second molecule of aniline, the indamine develops a second nitrogen linking and a phenazine containing a third bnezene ring is formed. This is phenosafranine, the simplest of the safranines, of the following constitution:

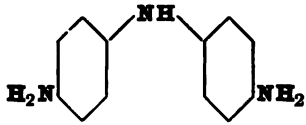


Phenosafranine.
Paraquinoid linking

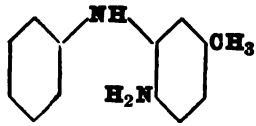


Phenosafranine.
Orthoquinoid linking

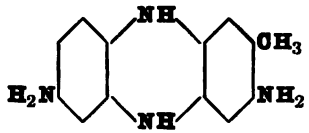
This phenosafranine is chiefly of theoretic interest; but it assists in understanding the constitution of safranine itself, which we may regard as a dimethylphenosafranine. Summarizing the progress thus far by a series of structural formulas, we have:



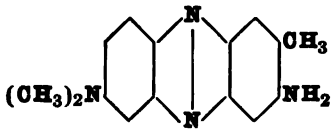
Leuco-indamine
or leuco phenylene blue



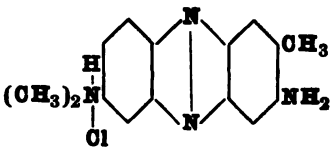
Leuco toluylene blue



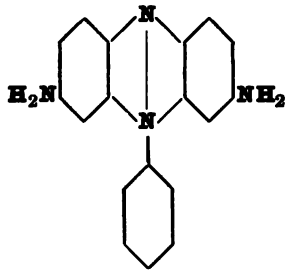
Leuco toluylene red. (Simplified form)



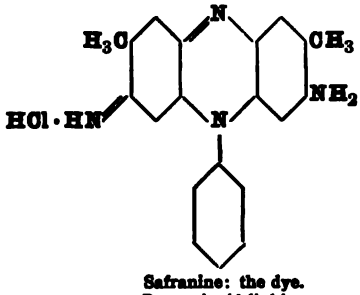
Toluylene red. Color base



Toluylene red. The dye

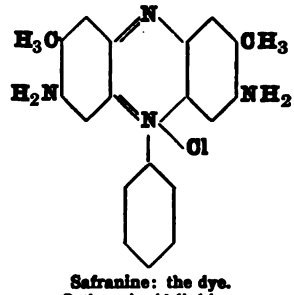


Phenosafranine. Color base



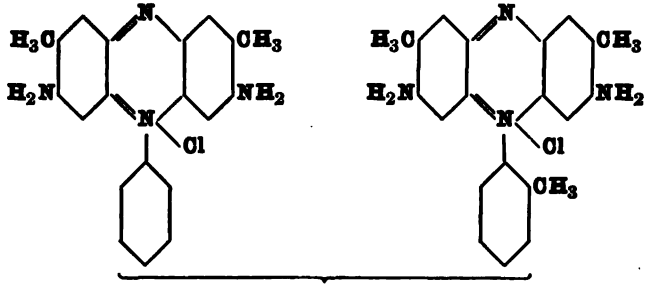
Safranine: the dye. Paraquinoid linking

or



Safranine: the dye. Orthoquinoid linking

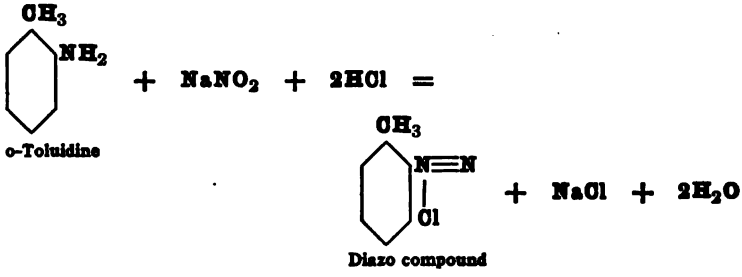
Safranine, the individual dye. This dye appears in commerce as a reddish-brown powder. In water, it dissolves easily with a red color; in alcohol, it yields a solution with a yellowish-red fluorescence. It is not a simple substance, but a mixture of the two bodies of the constitution shown here, which differ only in the first having a phenyl group, the second a tolyl group attached to the lower central nitrogen atom.

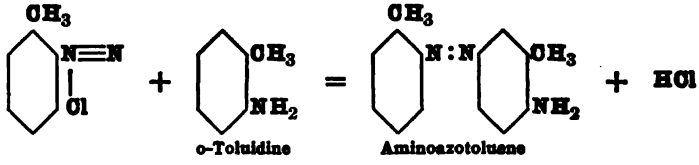


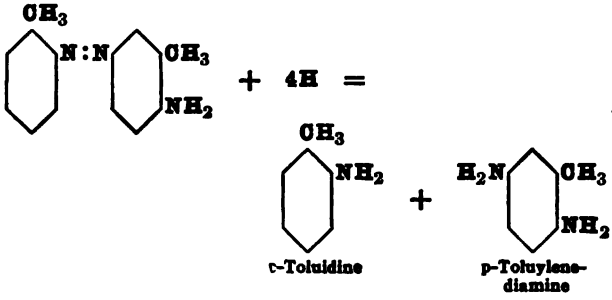
Commerical safranine

The present technical method for its manufacture consists in the oxidation of equal molecules of *p*-toluylenediamine and *o*-toluidine to the corresponding indamine and then the further condensation of this with one molecule of *o*-toluidine to form at last the desired safranine. The gradual progress of this reaction toward the end product will be observed below:

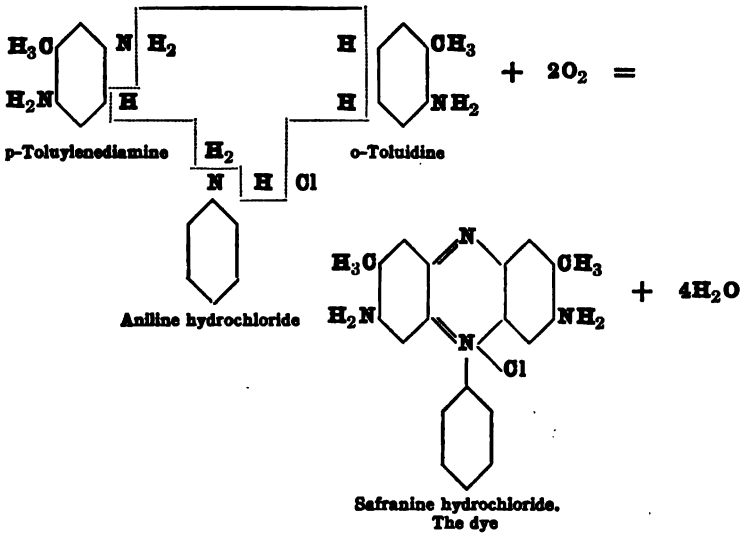
First the formation of *p*-toluylenediamine from *o*-toluidine by the diazo reaction is:







Then the condensation of the *p*-toluylenediamine with the *o*-toluidine and aniline follows thus:

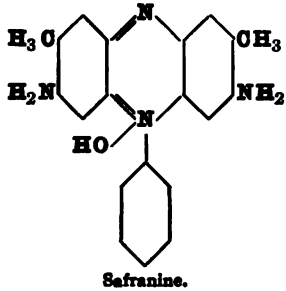


NOTE. If the aniline is replaced by a monoaklyl-*o*-toluidine, a safranine yielding a clearer shade of red in dyeing is formed.

Hydrochloric acid changes a safranine solution to a bluish color. Sodium hydroxide causes a brownish-red precipitate to fall. The solution in strong sulphuric acid is first green, and on dilution first blue and finally red. This is explained by the formation of an unstable green triacid salt in the strong acid, a decomposition by a little water into an unstable blue diacid salt, and on further dilution a further decomposition into the stable monacid salt which the addition of more water does not affect.

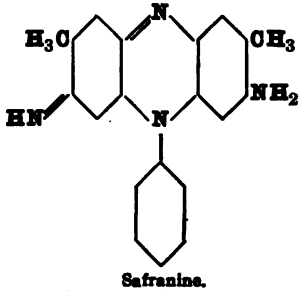
Safranine colors cotton but slightly and so is easily washed out; but, as a basic dye, it dyes cotton mordanted with tannin and tartar emetic red. It is employed in cotton printing, also to tone the shades of alizarine red. Silk is dyed to some extent; but the dye possesses less value in wool dyeing.

Safranine has been found to be poisonous. Th. Weil (Zeits. für Hygiene, 1891, p. 35), states that .05 gram of safranine hydrochloride per kilo weight is a fatal dose for a dog, injected hypodermically. A peculiar eruption of the skin has also been caused by a lining material dyed with safranine. The color base of safranine has the same color as the dye itself, and it is soluble in water with the same color. It may be prepared by adding barium hydrate to the solution of safranine sulphate. The strong basic property of this color base enables it to draw carbon dioxide from the air to form the carbonate. The color base has the constitution indicated:



Safranine.
Color base

or



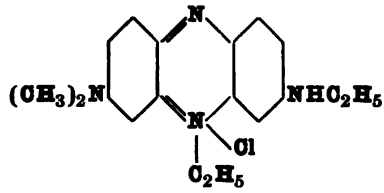
Safranine.
Anhydride of color base

The first formula exhibits the base as corresponding to ammonium hydroxide; but repeated crystallization from hot water has been found to produce a base free of the elements of water. This anhydrous base may be accounted for by a splitting off of a molecule of water and a readjustment to the paraquinoid constitution as shown in the second formula.

Fast Neutral Violet B. (1880), is a paste of bronze lustre or a bronze-colored powder, which gives a reddish-violet solution with both water and alcohol. It is prepared by the reaction of nitrosodimethylaniline upon diethyl-*m*-phenylene-diamine.

Nitrosodimethyl-aniline

Diethyl-m-phenylene-diamine

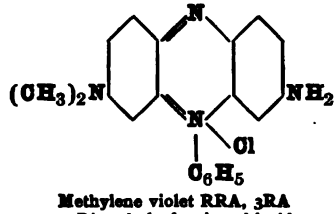


Fast neutral violet B.
m s-Ethyldimethylethyl-
phenazonium chloride

An excess of hydrochloric acid changes the solution from violet to blue. Sodium hydroxide has no effect until an excess has been added, when the dye is partially precipitated. Strong sulphuric acid dissolves the dye with a reddish-gray color; it then turns blue-violet on adding water and finally reddish-violet.

Fast neutral violet B dyes tannined cotton a fast violet, and it is only used for dyeing and printing this fibre.

Methylene Violet RRA, 3RA is a reddish-violet dye which is sold as a brown powder that is easily soluble in water or alcohol with a violet red color. Oxidation of dimethyl-*p*-phenylenediamine and aniline causes their union and forms the dye.



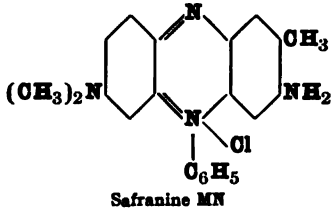
Methylene violet RRA, 3RA
a s-Dimethylsafranine chloride

Hydrochloric acid turns the solution bluish-violet, while sodium hydroxide causes a brownish-red precipitate to fall. Concentrated sulphuric acid forms with it a green solution which the gradual addition of water turns first blue and finally violet red.

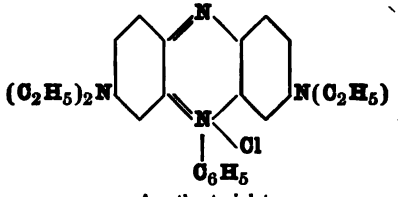
Tannined cotton is dyed reddish-violet. It is employed chiefly for cotton printing and is reasonably fast.

Safranine MN. appears as a black powder, which is soluble in water with a reddish-violet color. The reddish-violet solution in alcohol shows an orange fluorescence.

The substances brought together and caused to unite by oxidation to produce this dye are dimethyl-*p*-phenylenediamine with aniline and *o*- or *p*-toluidine. Its structure is given by the following formula:



Safranine MN
m s-Phenyl-a s-dimethyl
diaminotoluphenazonium chloride

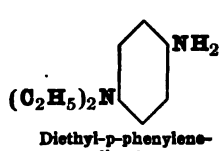


Amethyst violet.
Tetraethylphenosafranine

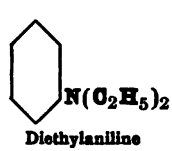
The reddish-violet aqueous solution is turned blue by hydrochloric acid, while sodium hydroxide produces a dark-red precipitate which dissolves in much water to a reddish-violet color.

Blue, green, and reddish-violet colors are made to appear in succession by dissolving the dye in strong sulphuric acid, and gradually adding water.

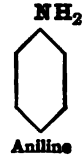
Amethyst Violet (1883), is a derivative of phenosafranine containing four ethyl groups symmetrically arranged in the molecule. The dye is made by oxidizing diethyl-*p*-phenylenediamine together with diethylaniline and aniline. The three constituents are arranged below in the relative positions they occupy in the completed dye molecule.



Diethyl-p-phenylene-diamine



Diethylaniline



Aniline

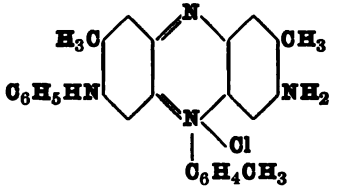
Amethyst violet is a blackish-gray powder whose aqueous solution is reddish-violet. The fuchsine red alcoholic solution displays a bluish-red fluorescence.

Hydrochloric acid converts it to blue color, while sodium hydroxide leaves it unchanged. Dilution of the green solution in strong sulphuric acid turns it blue and then bluish-violet. Silk is dyed a shade of violet which fluoresces to a reddish tone.

Mauve, Perkin's Violet has the unique distinction of being the first dye to be made from coal-tar products on a commercial scale. W. H. Perkin, in 1856, discovered it and put it upon the market in a form soluble only in alcohol. This expensive solvent limited its use to the dyeing the most costly of all fibres, silk. The shade was at once highly prized by the silk dyers and its appearance was the signal for the most astonishing activity and research by all European chemists. No single discovery in the field of chemistry can compare with this in its tremendous influence in opening and developing an entirely new and untried field.

Mauve has been long superseded by other dyes save for English postage stamps, which were colored with this mauve until the close of Queen Victoria's reign. More than a score of different trade names have been applied to it, of which the most appropriate was Perkin's violet.

The manufacture of mauve consisted in oxidizing a mixture of aniline and toluidine, when a derivative of safranine resulted.



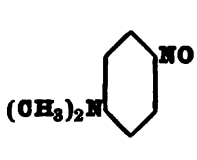
Mauve: Perkin's violet.
m s-Phenyltolusafranine chloride

Mauve was sold as a reddish-violet paste or reddish crystals, which were insoluble in cold water and only soluble with difficulty in boiling water to a reddish-violet solution.

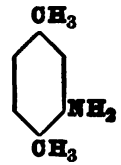
Hydrochloric acid does not affect the shade, but a bluish violet precipitate falls when sodium hydroxide is added. The olive green color in strong sulphuric acid is changed first to green when water is added, then to blue, and lastly to reddish-violet.

Mauve dyes silk a reddish-violet. It is used to whiten silk in the skein. Cotton may be dyed without employing a mordant. In fastness to light, mauve is superior to methyl violet.

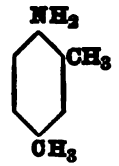
Heliotrope B, 2B is a safranine used in cotton printing to tone the shades of alizarine violet. The xylidines are required for its manufacture. It is prepared by coupling together nitrosodimethylaniline and a mixture of *m*-xylidine and *p*-xylidine hydrochlorides which react to produce heliotrope B, 2B. The factors and the product are grouped thus:



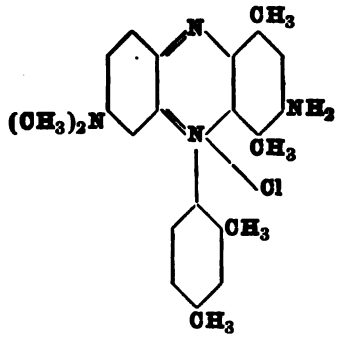
Nitrosodimethylaniline



m-Xylidine



p-Xylidene



Heliotrope B, 2B.

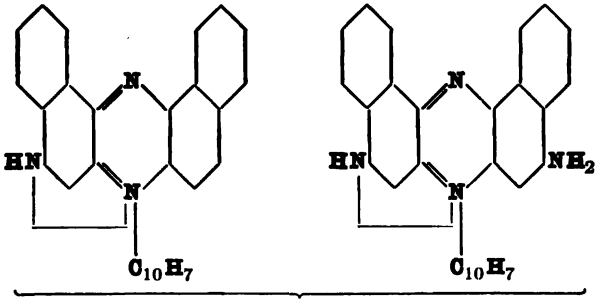
Heliotrope B forms a brown paste or a powder of a grayish-green color, which dissolves in both water and alcohol with a rosaniline color.

Hydrochloric acid leaves the color unchanged until a great excess has been added, when it turns blue. Sodium hydroxide causes a red precipitate to fall which, when filtered off, will dissolve in water. If dissolved in strong sulphuric acid, it passes through the shades of green, blue, and red on the gradual addition of water.

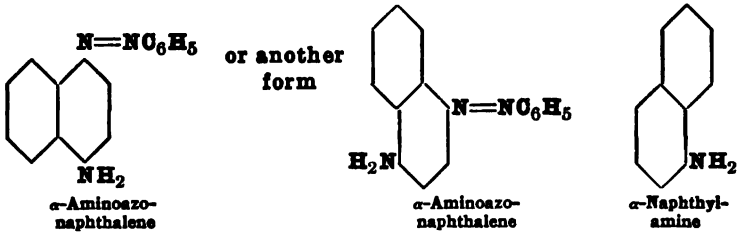
Cotton mordanted with tannin is dyed a reddish-violet.

Magdala Red (1868), is a beautiful dye whose high price limits its application to silk. Upon this fibre, it is used to produce the most delicate rose-red shades which exhibit a splendid fluorescence of a peculiar pearl-gray character. It is composed of two naphthalene rings joined by the azine group, i.e., the nucleus of the dye is so constituted. For its manufacture, the complex aminoazo compounds are employed, which must first be decomposed and then the products must recombine with the aid of added amino compounds.

Magdala red is made by the mutual reaction of the hydrochloride of aminoazonaphthalene with α-naphthylamine.



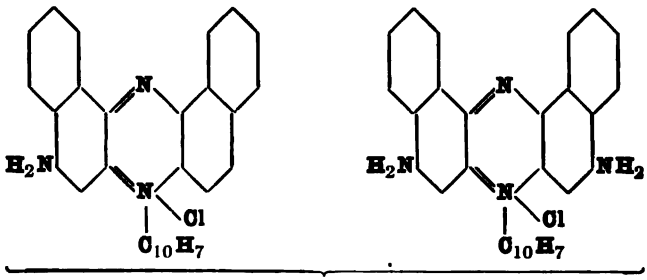
Magdala Red. Bases



α-Aminoazonaphthalene

α-Aminoazonaphthalene

α-Naphthylamine

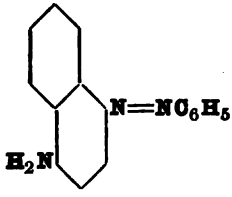


Magdala red

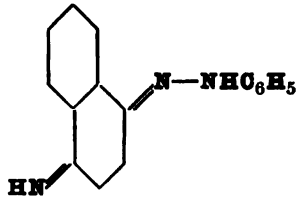
The question must arise as to the preliminary decomposition of the azo compound, so that the products obtained are available for recombining with the other amino compounds to form the dye itself.

An instance of such decomposition and rearrangement may be shown by the formation of a similar dye through the fusion of aminoazonaphthalene with aniline and aniline hydrochloride.

The aminoazonaphthalene passes first into the isomer hydrazone.

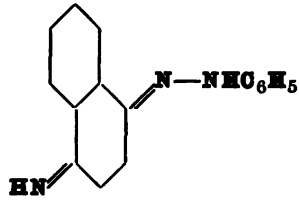


α-Aminoazonaphthalene

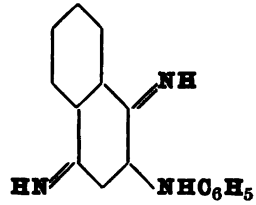


Hydrazone

By a migration of the aniline residue from the side chain into the main ring, we obtain a compound available for union with the other components.

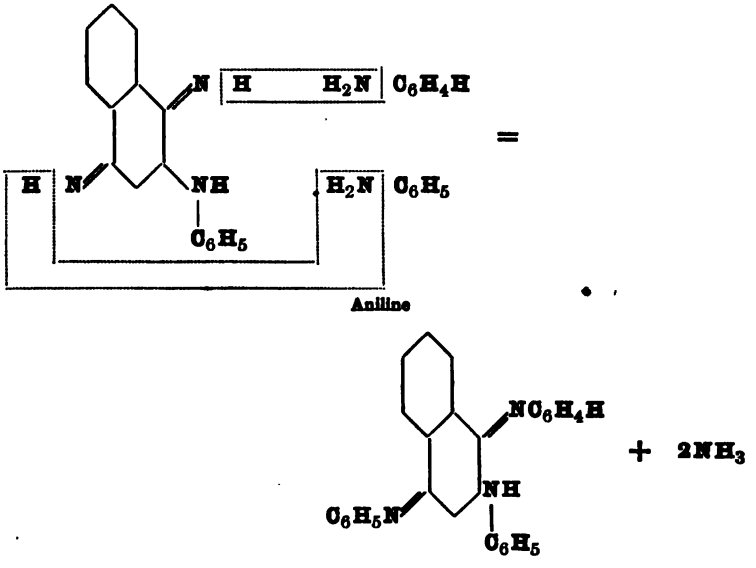


Hydrazone

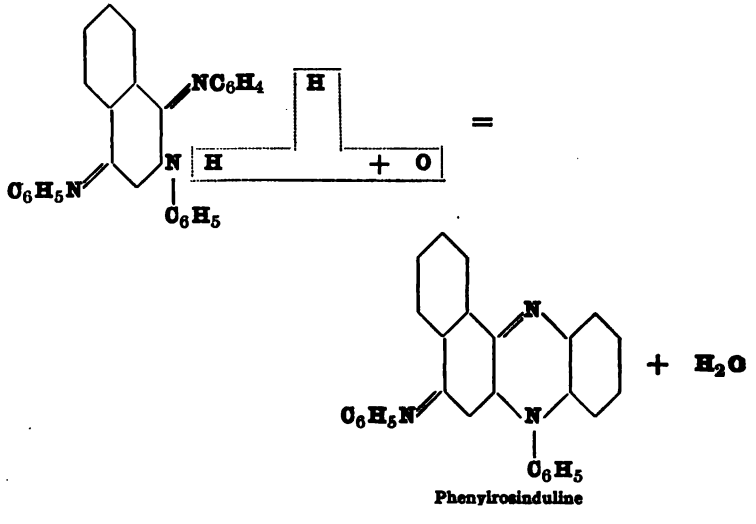


Anilidoquinonediimide

It is now in condition to unite with aniline with the elimination of ammonia.

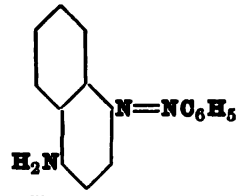


By oxidation an azine ring is developed and the dye is formed

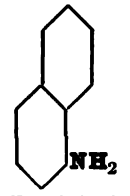


Milling Blue (1890), is a naphthylsafranine, which unlike the safranines in general is not used for cotton dyeing. On the contrary, it is used for dyeing wool which has been treated with chromium mordant.

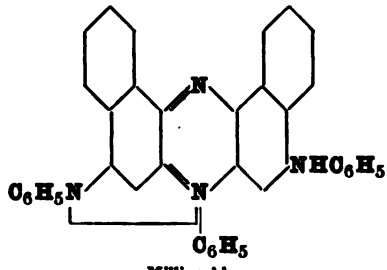
Milling blue is the product of melting together anilineazo-α-naphthylamine with the hydrochloride of α-naphthylamine and aniline.



Anilineazo-α-Naphthylamine



α-Naphthylamine



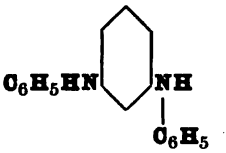
Milling blue

Milling blue is a bronze-colored powder which forms a blue solution in water.

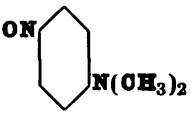
Hydrochloric acid causes a blue precipitate to fall while sodium hydroxide turns the solution bluish black. The bluish-green solution which it makes with strong sulphuric acid turns blue when water is added. Wool which has been mordanted with chromium salts is dyed blue.

Indazine M is a beautiful blue dye so closely related to mauve that it is often called pseudo-mauve. The dye is the hydrochloric acid salt which yields a blue solution with water and also with alcohol. The base itself is soluble in water with a red color.

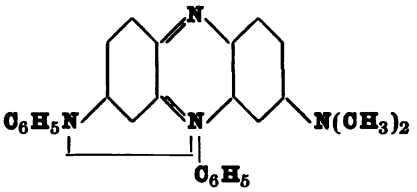
Indazine M is prepared by bringing together nitroso-dimethylaniline and diphenyl-*m*-phenylenediamine when the indazine is formed.



Diphenyl-m-phenylenediamine



Nitrosodimethylaniline



Indazine M.

Indazine M has the appearance of a blue powder. Hydrochloric acid turns its solution bluer and sodium hydroxide gives a blue precipitate. A blackish solution is formed with concentrated sulphuric acid which dilution with water turns to blue.

Cotton when mordanted with tannin is dyed blue which is fast to washing and furthermore is not affected by acids and alkalies.

The dye is not a homogeneous substance. It contains an ingredient of a more greenish-blue shade which is believed to be the result of the further action of nitrosodimethylaniline on the true indazine.

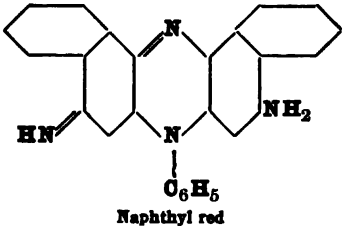
Naphthyl Dyes

Three dyes, a red, a violet, and a blue have been placed upon the market which produce valuable fluorescent shades upon silk.

Their structure is of peculiar interset since a comparison of

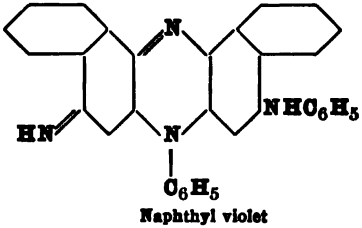
their constitutional formulas allows us to see how the color of a dye is influenced by the entrance of additional phenyl groups into the dye molecule.

Naphthyl red is a naphthosafranine.



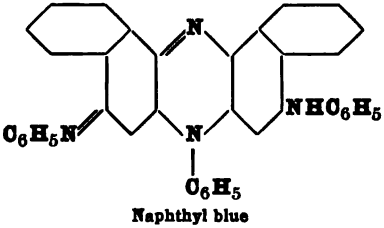
Naphthyl red

If one of the hydrogens of the amino group in this molecule is exchanged for a phenyl group, then the red color turns to violet.



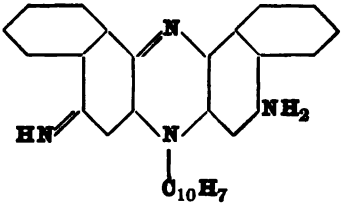
Naphthyl violet

Now when the hydrogen of the imino group is replaced by a phenyl group, the color is converted from violet to blue.



Naphthyl blue

The naphthyl red recalls the magdala red described above, which differs only in having a naphthyl instead of a phenyl group attached to the central or azine nitrogen.

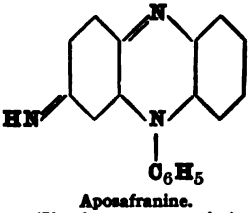


Magdala red

The Aposafranines

The dyes classed as the aposafranines are of simpler structure, in possessing one amino group in place of two, than the safranines, and yet their discovery was later. The study and elucidation of their constitution was nearly parallel with the investigation of the safranines. The two classes bear so close a relation to each other that many of the facts brought slowly to light were of mutual assistance in solving their structure and in arriving at rational formulas for both.

The constitution of aposafranine is apparent from the formula below:



Aposafranine.
(Simplest representative)

Aposafranine is at once seen to contain three benzene rings to the central azine group and therefore it falls into the class of the azine dyes. No dye of this class, however, has in reality so simple a constitution as represented above; for in these dyes, a naphthalene group is always present.

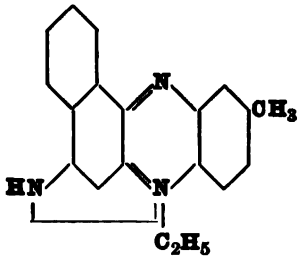
If the imino group is affixed to the naphthalene nucleus, then the special name of rosinduline is given to it. If, on the contrary, the imino group located in the benzene ring, it is

called an *iso*rosinduline. A difference in color results according to the location of this imino group.

Aposafranines { Rosinduline: Chiefly shades of red. / *Iso*rosindulines: Chiefly shades of blue and green.

Rosindulines. Induline scarlet as a rosinduline contains the imino group in the naphthalene nucleus of the dye molecule.

Induline scarlet is prepared by melting together azo-derivatives of monoethyl-*p*-toluidine and a naphthylamine hydrochloride.



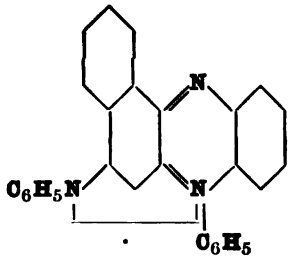
Induline scarlet

Induline scarlet is a red powder which is soluble in water, with a red color, and in alcohol with an orange color exhibiting a yellowish fluorescence.

No change is caused by adding hydrochloric acid. Sodium hydroxide precipitates a resinous violet-colored body. The solution in strong sulphuric acid is a wine red, which by adding water passes through green to red.

Cotton mordanted with tannin is dyed scarlet red. It is used principally for cotton printing.

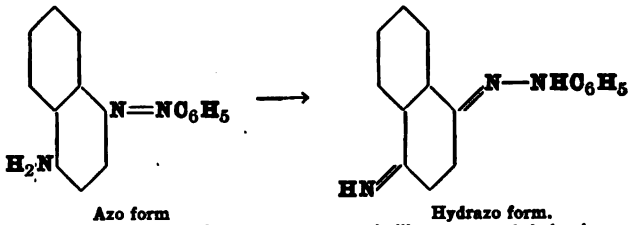
Azocarmine G is a red paste with a lustre of gold which dissolves with difficulty in water and communicates to it a bluish-red color. In its manufacture, phenylrosinduline is first formed and by fuming sulphuric acid this is converted into a disulpho acid of which the sodium salt forms the commercial dye. The process consists in melting together aniline-azonaphthylamine and aniline, and aniline hydrochloride.



Phenylrosinduline.
Base of azocarmine G.

As an example of the readjustment which is believed to take place in the complex anilineazonaphthalene before it can form a union with aniline to produce the dye, the following reactions may be given:

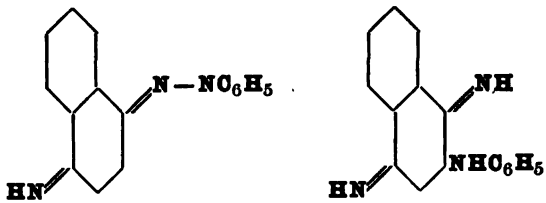
First, the aminoazo compound changes its forms from an azo to a hydrazo compound by the shifting of a hydrogen atom from the amino group to the azo group as follows:



Azo form
Anilineazo-α-naphthylamine

Hydrazo form.
Anilineazo-α-naphthylamine

The azo group then breaks up; the anilido group $-NHC_6H_5$ changing position with the neighboring hydrogen atom, thus producing anilidonaphthoquinonediimide.

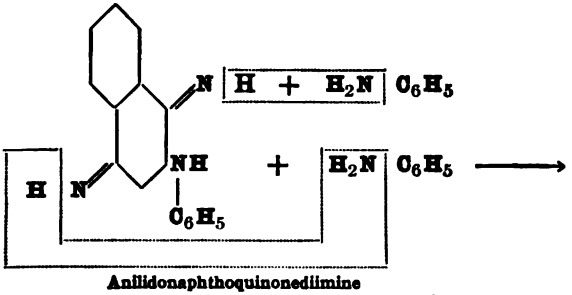


Hydrazo form

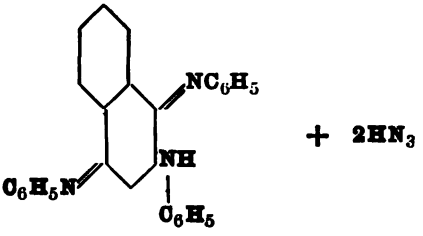
Anilidonaphtho-
quinonediimide

Now the action of two molecules of aniline upon this substance which has undergone a double transformation

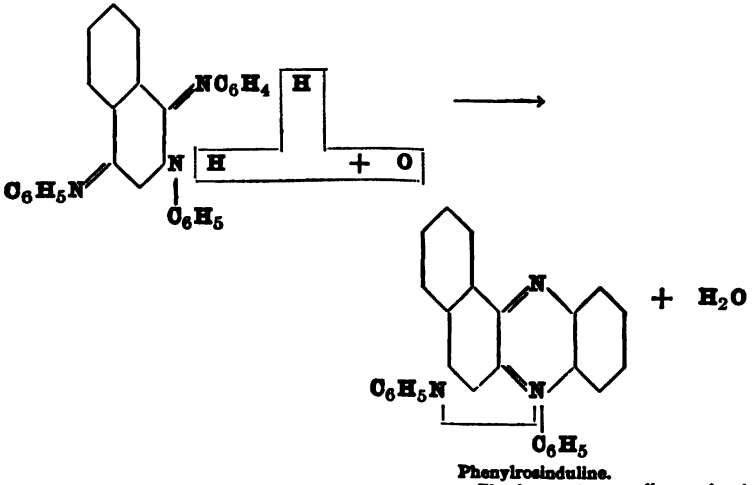
before it is ready to act, produces phenylrosinduline as follows:



Anilidonaphthoquinonediimine



The action of oxygen is now necessary to remove two hydrogen atoms and form the azine ring.



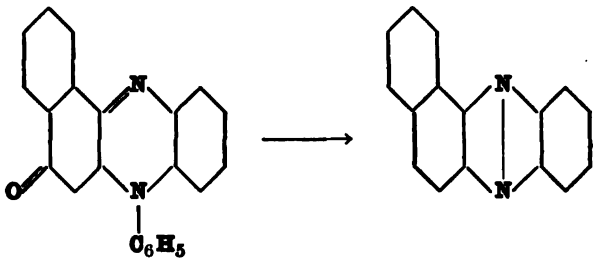
Phenylrosinduline.
The base whose sodium salt of the disulpho acid is the dye azo-carmine G.

Azocarmine G in its bluish-red aqueous solution yields a red precipitate on adding hydrochloric acid; this precipitate is, however, soluble in water; sodium hydroxide produces no change. In concentrated sulphuric acid, it dissolves with a green color and the addition of water to this solution causes a red precipitate to fall.

Wool is dyed an even and fast bluish-red, which is pretty fast to light and not sensitive to acids and alkalies.

It is employed for producing mixed shades.

Rosinduline 2G. By treating azocarmine G, which is a disulpho acid, with fuming sulphuric acid, it is converted into a trisulpho acid. When this trisulpho acid is heated with water to 160–180°, a phenylamine group is replaced by oxygen and aniline is eliminated. Rosinduline 2G is the result. This is the sodium salt of rosindone monosulpho acid.



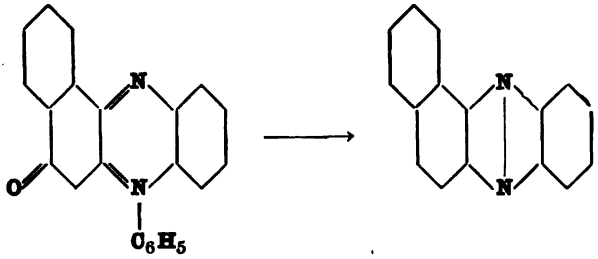
Rosindone — α-Naphthophenazine

Rosinduline 2G is a scarlet powder, which water dissolves with a scarlet red color.

From the aqueous solution, a yellow precipitate falls if hydrochloric acid be added. A scarlet precipitate is caused by sodium hydroxide. The solution in strong sulphuric acid is a dirty green color; but when a moderate amount of water has been added and some time has elapsed, a deposit of golden yellow crystals separates out.

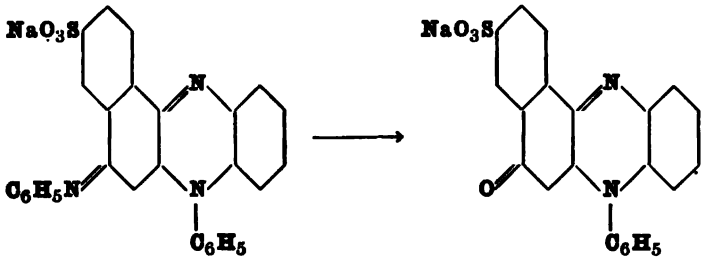
Both wool and silk are dyed an orange-red, from an acid bath, and the color is fairly fast to washing and milling. It also shows good resistance to acids and alkalies. The dye equalizes so well that goods may be at once placed in a boiling bath of the dye.

If this base rosindone be distilled and the vapor passed over zinc dust kept at a red-heat, oxygen and a phenyl group are split off, leaving the well-known naphthophenazine; thus proving the constitutional formulas ascribed to phenyl-rosinduline and rosindone.



Rosindone — α-Naphthophenazine

Rosinduline G. is a red powder which dissolves in warm water with an orange red color. This solution gelatinizes on cooling and standing. The dye is made by heating the sodium salt of phenylrosindulinenaphtho-6-monosulpho acid with water under pressure.



Rosinduline G.

This is a valuable acid dye for wool and silk.

The effects of hydrochloric acid and sodium hydroxide are the same as for rosinduline 2G.

The dirty green solution in strong sulphuric acid gives a brownish precipitate on diluting with water.

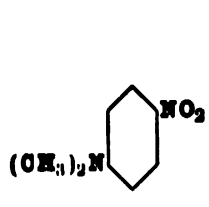
The scarlet which it dyes upon silk has the same properties as rosinduline 2G.

The Isorosindulines

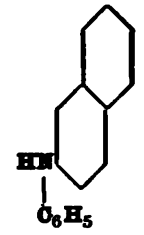
This class of the aposafranines differs from the rosindulines in having the substituted amino groups attached to the benzene as well as to the naphthalene nucleus.

The *iso*rosindulines differ further in being blue and green dyes while rosindulines are shades of red.

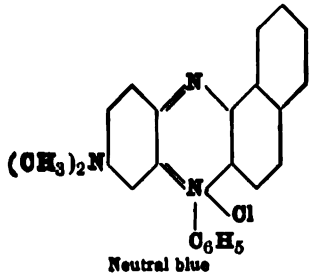
Neutral blue is prepared by allowing the hydrochloride of nitrosodimethylaniline act upon phenyl-β-naphthylamine.



Nitrosodimethyl-aniline



Phenyl-β-naphthylamine



Neutral blue

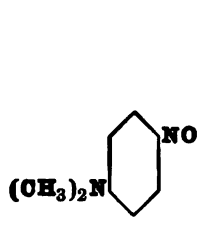
Neutral blue forms a dull brown powder which is easily soluble in water and in alcohol with a violet color.

No change occurs on adding hydrochloric acid save when a large excess is used; the shade is then a little bluer. Sodium hydroxide gives a violet precipitate. The brownish violet in strong sulphuric acid turns violet with addition of water.

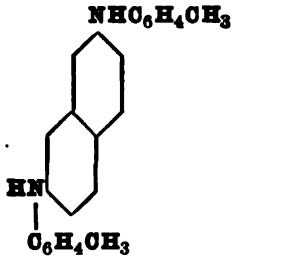
Cotton mordanted with tannic acid is dyed a blue which is useful for mixed shades. It is not suitable for wool or silk nor does it long resist the action of light or soap.

Basle blue R. is another blue dye of the *iso*rosindulines. It is a brown crystalline powder, and it dissolves in water with a bluish-violet color. If zinc dust is warmed with the solution, the color disappears; but it becomes blue again by exposure to the action of the air.

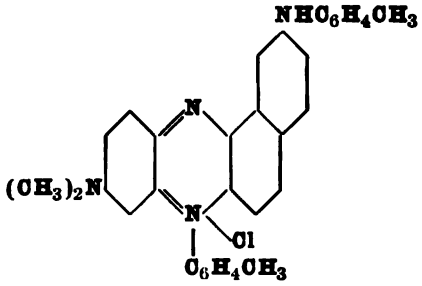
Basle blue R. results from the action of the hydrochloride of nitrosodimethylaniline upon 2.7 ditolylnaphthalenediamine.



Nitrosodimethylaniline



2:7-Ditolylnaphthalenediamine



Basle blue R.

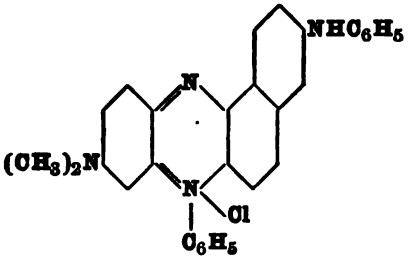
If to the bluish-violet aqueous solution of this dye hydrochloric acid is added, a blue precipitate falls while a bluish-black precipitate is caused by sodium hydroxide.

In strong sulphuric acid, the dye dissolves to a greenish-brown solution, then upon gradual addition of water, a change to green first occurs succeeded by a violet, followed by the separation of a bluish-violet precipitate.

Cotton mordanted with tannin and tartar emetic is dyed blue. This dye has been largely superseded by indoine blue.

Azine Green G.B. This dye is of interest in allowing us to see the effect of removing two methyl groups and a sliding of an amino group in basle blue R. The color changes consequently from blue to green. The methyl groups were situated in two separated benzene rings, thus making them tolyl groups.

Azine green G.B. is made by the action of nitrosodimethylaniline upon 2.6. diphenylnaphthylenediamine.



Azine green G.B.

Azine green G.B. is a dark-green powder which is soluble in both water and alcohol with a green color. Green precipitates fall either on adding hydrochloric acid or sodium hydroxide.

Concentrated sulphuric acid dissolves the dye to a brownish solution, but the color turns to green on adding water.

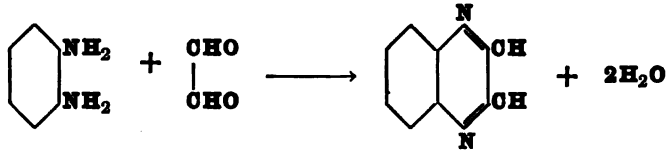
Cotton mordanted with tannin is dyed dark green.

CHAPTER XIII

THE QUINOXALINE, QUINOLINE, AND ACRIDINE DYES

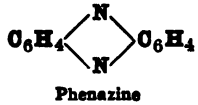
The Quinoxaline Dyes

The quinoxalines were discovered by Hinsberg, who applied the term as a general name for the products he obtained by the action of diketones upon *o*-diamines. The simplest representative is a pure quinoxaline from *o*-phenylenediamine and glyoxal.



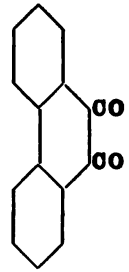
o-Phenylene-diamine — Glyoxal — Quinoxaline

Later those compounds of purely aromatic character were termed azines, of which phenazine is the simplest example,

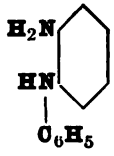


Phenazine

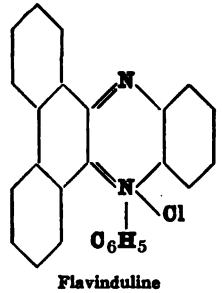
Flavinduline is the only important dye of this class and it has the peculiarity of possessing no auxochromous group. It is formed by phenanthrenequinone acting upon *o*-amino-diphenylamine in glacial acetic acid.



Phenanthrene-quinone



o-Amino-diphenylamine



Flavinduline

It may be seen from the formula that the flavinduline has phenazine as a nucleus.

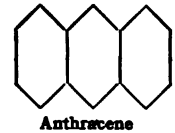
Flavinduline is a powder of a color between a brownish yellow and an orange red. Its aqueous solution is orange red. No change is caused by hydrochloric acid, but a grayish green precipitate is caused by sodium hydroxide, and this later turns to a grayish yellow.

Quinoline Dyes

Quinoline resembles both benzene and pyridine, for it consists of a benzene nucleus and a pyridine ring joined. It may be regarded as naphthalene in which a carbon and hydrogen of the latter have been replaced by a nitrogen atom. Acridine bears to quinoline the same relation that anthracene does to naphthalene. Indeed the analogy between the three nitrogenous substances pyridine, quinoline, and acridine and the hydrocarbons, benzene, naphthalene, and anthracene may easily be seen from the following skeleton formulas of the two series:

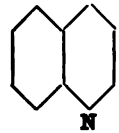
Benzene

Naphthalene

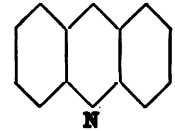


Anthracene

Pyridine



Quinoline

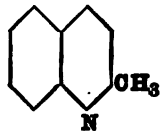


Acridine

Quinoline is a colorless liquid with a high boiling-point (239°), possessing a characteristic disagreeable penetrating odor and a high refractive power. The nitrogen is responsible for its basic properties, through which it is able to form salts with acids. It turns brown on exposure to the air.

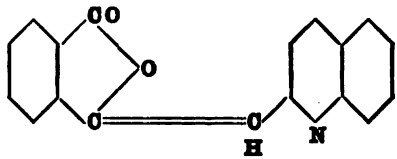
Quinoline is present in coal-tar, in the oil obtained by the distillation of bones, in "stupp" fat obtained from distillation of the bituminous mercury ores of Idria. It may be made synthetically by the celebrated Skraup method of heating together nitrobenzene, aniline, glycerine and sulphuric acid.

Quinoline yellow: spirit soluble (1882) is made from a methyl derivative of quinoline called quinaldine, wherein the methyl group stands attached to the carbon atom next to the nitrogen in the pyridine ring.



Quinaldine or
α-methylquinoline

When quinaldine is heated with phthalic anhydride, two hydrogens from the methyl group of the quinaldine unite with an oxygen atom from the anhydride to separate as water, while the union of the residues produces the quinoline yellow. In the formula, the double bond indicates the point of union subsequent to the removal of the molecule of water.



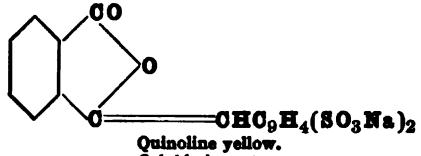
Quinoline yellow.
Soluble in spirit

Quinoline yellow is a yellow powder which water will not dissolve, while alcohol dissolves it with difficulty to a yellow solution.

Concentrated sulphuric acid dissolves it, forming a yellowish red solution, but the addition of water causes the separation of the dye as a yellow flocculent precipitate.

Spirit varnishes and waxes are dyed yellow. It is used for making the soluble quinoline yellow.

Quinoline yellow: water soluble (1882) is made from the spirit-soluble quinoline yellow just described, by the action of fuming sulphuric acid. Two sulphonic acid groups (—SO_3H) become fixed in the quinaldine portion of the molecule. The sodium salt of this disulphonic acid is the dye:



Quinoline yellow.
Soluble in water

The position of the two sulphonic acid groups is as yet uncertain.

This dye is a yellow powder which is easily soluble in both water and alcohol with a yellow color. Hydrochloric acid simply brightens it while caustic soda darkens it. The yellowish red solution in strong sulphuric acid turns yellow on addition of water.

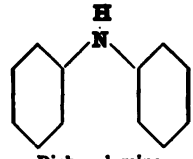
Wool and silk are dyed a prized shade of greenish yellow in an acid bath. It replaces the yellow dye picric acid. The color is very fast to light and is not sensitive to acids and alkalies; it is less fast to washing and milling.

Its widest application is in silk dyeing. Reducing agents do not affect it.

Acridine Dyes

Acridine, which gives its name to a few yellow and orange dyes of this group, is basic in its nature. It is a solid which crystallizes in colorless needles, which may be sublimed. Upon the skin and mucous membranes it has an intensely irritating effect. Crude anthracene and crude diphenylamine contain acridine in small amounts. Dilute solutions of its salts show a greenish blue fluorescence.

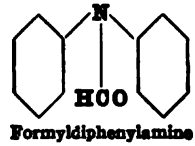
The structure of acridine may be proved to consist of two benzene rings which are united in ortho positions of union by a nitrogen atom and a carbon atom, and it may be prepared synthetically from diphenylamine and formic acid. Diphenylamine contains two benzene rings joined by a nitrogen atom which in turn hold a hydrogen as shown below:



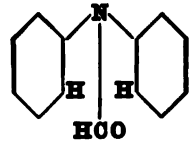
Diphenylamine

Formic acid

When this is treated with formic acid, the hydrogen attached to the nitrogen together with the hydroxyl of the formic acid unite to produce water, while the formyl group (HCO) affixes itself to the nitrogen, yielding formyldiphenylamine.

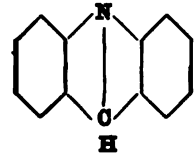


Formyldiphenylamine



Formyldiphenylamine

Zinc chloride acting upon this removes the oxygen from the formyl group and a hydrogen from each benzene ring in the form of water, and a molecule of acridine is produced.

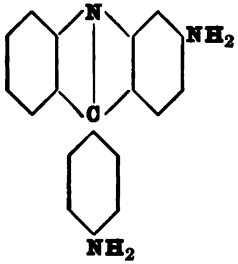


Acridine

Acridine may now be seen to consist of three six-membered rings, the middle one containing a single nitrogen. This single nitrogen has sufficient influence to impart to the whole molecule a basic character whereby it forms salts with acids. By comparison with alizarine, a very close resemblance is apparent, since a replacement of the single nitrogen atom by a carbon with an attached hydrogen atom would at once convert acridine into alizarine.

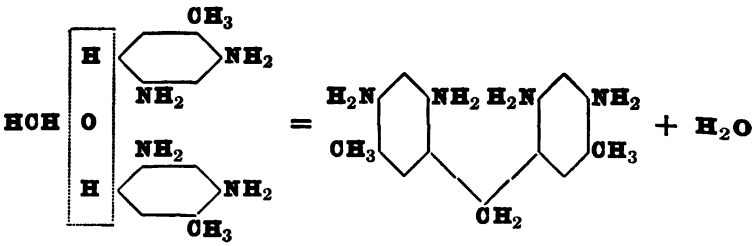
Some acridine products were formed as impurities during the manufacture of rosaniline from aniline and toluidine.

For example, chrysaniline and crude commercial chrysaniline, known as phosphine, were obtained from the waste material left from the rosaniline melt when the arsenic process was employed. These dyes are more or less impure forms of diaminophenyl acridine.



Diaminophenyl acridine

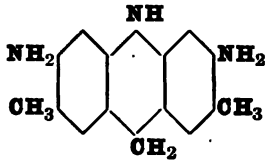
Acridine Yellow. When *m*-toluylenediamine is treated with formaldehyde a condensation of three molecules into one results, with the separation of water as shown below:



Formaldehyde m-toluylene-diamine

Tetraaminoditolylmethane

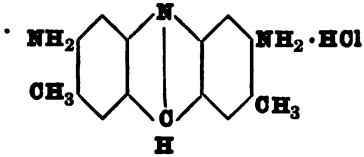
It will be noticed that if this new substance could lose ammonia from the amino groups which are nearest together a third closed ring would be formed and a product resembling acridine would result. Hydrochloric acid acts upon it, splitting off ammonia as follows, forming diaminodimethylhydroacridine.



Diaminodimethyl-hydroacridine

Oxidation of this intermediate product removes a hydrogen atom from the middle nitrogen and the middle carbon and causes the union of these two atoms across the ring, thus forming the dye acridine yellow, which is sold in the form of hydrochloric acid salt.

In commerce, it is a yellow powder which dissolves with a yellow color and a greenish flourescence in both water and alcohol.



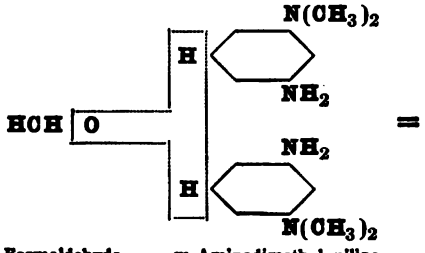
Acridine yellow hydrochloride

Both hydrochloric acid and sodium hydroxide cause a yellow precipitate to fall. In strong sulphuric acid it forms a bright yellow solution from which addition of water causes a yellow precipitate to deposit.

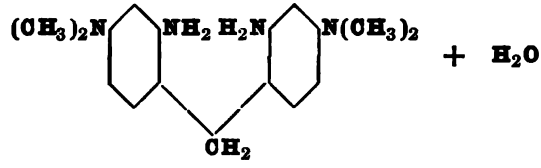
Silk is dyed a greenish yellow with a greenish fluorescence. Cotton mordanted with tannin is dyed yellow.

Acridine Orange NO is prepared in a manner similar to that for acridine yellow save that the substances used to condense with formaldehyde are somewhat different. Formaldehyde is brought together with two molecules of *m*-amino-

dimethylaniline when a condensation with elimination of water takes place as follows:

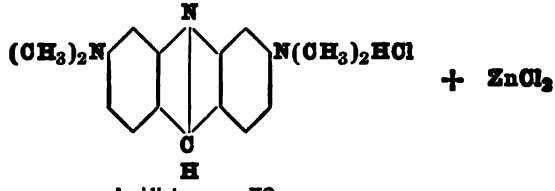


Formaldehyde m-Aminodimethylaniline



Tetramethyltetraaminodiphenylmethane

This product separates a molecule of ammonia on treatment with hydrochloric acid and a closed central ring is formed. Subsequent oxidation removes two hydrogens as explained under acridine yellow and then the product is acridine orange NO. The hydrochloride of this is the commercial form and it usually appears crystallized with one molecule of zinc chloride, as shown below:



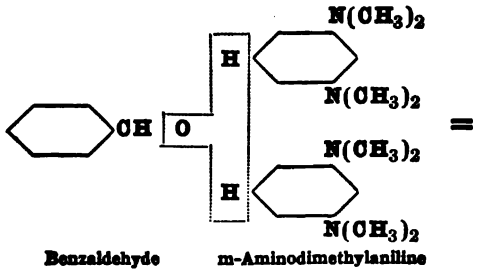
Acridine orange NO

The dye is an orange-colored powder which dissolves to form an orange yellow solution with a greenish fluorescence in both water and alcohol. Hydrochloric acid turns the solution red. Sodium hydroxide causes a yellow precipitate. Its solution in strong sulphuric acid is almost colorless though it possesses a greenish fluorescence; addition of water turns this solution orange at first, then red.

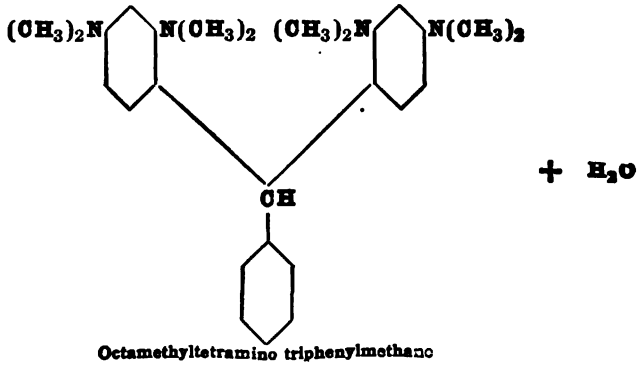
Cotton mordanted with tannin is dyed orange. Silk in a boiled-off soap bath is dyed orange with a greenish fluorescence. It is moderately fast to light and to the action of soap.

Acridine Orange R. Extra. In this dye, the effect of the addition of a phenyl group upon the shade of a color may be observed. The only difference between this dye and acridine orange NO is a phenyl group which replaces the hydrogen atom attached to the central carbon atom of the molecule. This changes the orange dye to an orange red dye.

To secure this difference in composition, it is only necessary to select benzaldehyde in place of formaldehyde, where the requisite phenyl group is brought into the reaction at the beginning. One molecule of benzaldehyde is condensed with two molecules of *m*-aminodimethylaniline; this is carried on in an alcoholic solution by aid of the dehydrating action of hydrochloric acid.

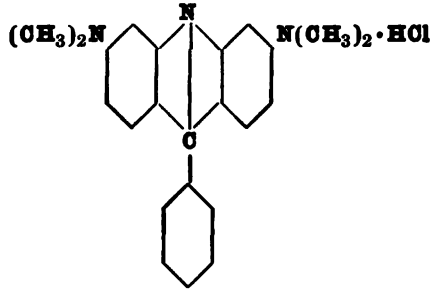


Benzaldehyde m-Aminodimethylaniline



Octamethyltetramino triphenylmethane

From this product a molecule of ammonia is separated, forming a closed ring central, with the result of yielding the leuco compound of the dye; when by oxidation two hydrogen atoms are removed, the linking of the central nitrogen and carbon atoms occurs and the dye is produced. The hydrochloric acid salt is the commercial form of the dye and its constitution is shown below:



Acridine orange R. extra

It appears in commerce as an orange red powder which gives an orange yellow solution, while in alcohol, in addition to the orange yellow color, there appears a greenish fluorescence. Hydrochloric acid turns it red, while sodium hydroxide produces a yellow precipitate.

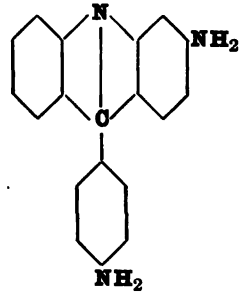
In concentrated sulphuric acid the solution is yellow with a green fluorescence, while an addition of water turns it red. Cotton is dyed orange red by aid of a tannin mordant.

Leather Yellow, Phosphine N., Phosphine P. In the manufacture of rosaniline or fuchsine by the arsenic acid oxidation process a large amount of waste product was formed. This was of the nature of a dye and being too valuable to throw away was worked up and put on the market under a variety of names, e.g., maroon, grenadine, geranium, cerise, juchtenroth, scarlet-cardinal, camelia, amaranth, Russian red, fuchsine scarlet, fuchsine ponceau, fuchsine yellowish, etc. These different names were used by various firms for practically the same product—an impure phosphine.

Research upon phosphine proved it to be mainly the substance known as chrysaniline, which is a derivative of acridine.

The waste product from the rosaniline manufacture contained mauve aniline, chrysaniline, rosaniline, violaniline and resinous matters. The process of extracting the chrysaniline was more or less difficult and tedious. By boiling with hydrochloric acid the violaniline and resinous matters remained insoluble and could therefore be separated. The rosaniline remaining was destroyed by reduction with zinc to its leuco compound.

The chrysaniline which thus made up the bulk of the phosphine was an unsymmetrical diaminophenylacridine of the following constitution:



Phosphine P.
Leather yellow

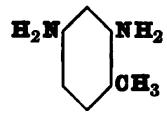
It comes into commerce as orange yellow powder which communicates a reddish yellow color with a yellowish green fluorescence to its solution in both water and alcohol. Hydrochloric acid is without action while sodium hydroxide produces a bright yellow precipitate. Concentrated sulphuric acid will dissolve it with a bright yellow color and a greenish fluorescence, from which addition of water produces a reddish yellow solution.

Leather yellow is used especially for dyeing leather; it is also employed for printing upon woolen goods. Cotton is dyed yellow by the assistance of a mordant and the color is moderately fast to soap but not to light.

Benzoflavine is a yellow dye for mordanted and unmordanted cotton. For silk and wool it is of less importance. As in the other acridine dyes, we have here the action of an aldehyde producing a condensation of two molecules of a diamine so as to yield acridine as a nucleus with various substituting groups.

One molecule of benzaldehyde reacts with two molecules of *m*-toluylenediamine. From the relative positions of the molecules as they are placed below, it may easily be seen how its three molecules become joined by the elimination of a molecule of water and one of ammonia.

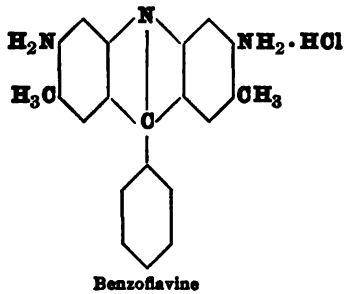
m-Toluylene diamine



m-Toluylene diamine

Benzaldehyde

Oxidation and union with an acid of the intermediate product formed above yields the completed dye benzoflavine.



Benzoflavine

Benzoflavine appears as brownish orange yellow powder which dissolves slightly in cold but easily in hot water to which it communicates a yellowish green fluorescence.

An orange-colored precipitate falls where hydrochloric acid is added and a yellowish white one when caustic soda is added. In concentrated sulphuric acid it dissolves, exhibiting strong green flourescence; this solution turns yellow and finally yields an orange precipitate as water is gradually added.

CHAPTER XIV

ANILINE BLACK

FROM aniline alone, one of the simplest coal-tar derivatives, there has been produced for years by one of the easiest processes of oxidation a black dye which is one of the most valuable in the whole range of synthetic colors. The qualities which have won for aniline black so high a degree of esteem are its great resistance to the action of soap, light and air. Furthermore, it resists successfully the action of weak chlorine, though strong chlorine converts it into a reddish brown.

Although the method of applying this dye to fabrics was discovered by Lightfoot in 1863 and within the first decade of the manufacture of synthetic dyes, the constitution of this color has in spite of the long-continued research of many investigators failed of a satisfactory solution. Recently Willstaeter and Moore claim to have discovered its constitution.

One of the marked properties of ordinary aniline is its tendency to turn rapidly on exposure to the air from a colorless liquid to a brown one. The process of converting aniline into a black dye consists in using oxidizing agents to hasten the progress of the oxidation toward black insoluble dye.

Among the oxidizing agents employed are manganese peroxide, lead peroxide, chromic acid, ferric salts, potassium ferrocyanide, permanganic acid, chloric acid and chlorates in the presence of metallic salts. Of the metallic salts, those of copper and vanadium are most efficient and most appreciated.

The function of these substances is to withdraw hydrogen from the aniline by oxidizing it away, leaving the aniline residues to join together and form the dye.

It is of interest to note when chlorates and metallic salts are employed for oxidation how small a quantity of the metallic salt is necessary to oxidize large amounts of aniline. The most remarkable of all of the metals is vanadium. According to Witz, part of vanadium with the aid of the required amount of potassium chlorate will suffice to convert 270,000 parts of aniline salt into aniline black. After vanadium follow in the order of their efficiency cerium, copper and iron; iron is noticeably weaker in its action than the others.

From these facts the conclusion is drawn that the metallic salts simply play the part of oxygen carriers. Only those metals are effective which have two states of oxidation. It therefore appears that the metallic salts in their higher state of oxidation act upon the aniline; when thus reduced to a lower state they are again raised by the chlorate present to the higher state and again become active upon more aniline. As evidence of the correctness of this view, it has been shown that when cupric chloride has been used with an insufficient amount of potassium chlorate cuprous chloride is present in the mixture.

Aniline black is an insoluble substance of a basic nature which in its free state is a dark violet to black in color. The salts formed by union with acids are, however, a dark green. These salts are unstable compounds and are by washing with water partly decomposed, and yet the removal of the whole amount of the acid is accomplished with difficulty.

Aniline black is insoluble in almost all solvents. It does nevertheless dissolve in aniline with difficulty to a violet color; on standing this violet shade passes over into a brown. Phenol dissolves it more easily with a bluish green color.

If the insoluble aniline black is treated with fuming sulphuric acid, different sulpho acids are formed, according to the strength of the acid and the time it is allowed to act. These free sulpho acids are green, while their easily soluble alkali salts are of a dark violet.

When submitted to reducing agents, aniline black forms an insoluble leuco compound which in a strong acid solution is slowly oxidized to the original aniline black. In an alkaline

solution the same reaction proceeds very rapidly. If strong reducing agents are employed; as for example tin and hydrochloric acid, a complete splitting up of the molecules occurs. The decomposition products include para-phenylenediamine, para-diaminodiphenylamine and diphenylamine. These facts, coupled with knowledge that energetic oxidation converts aniline black almost completely into quinone, leads to the conclusion that during the condensation of the aniline to aniline black, the nitrogen of one aniline radical must attach itself to the benzene ring of another and further more in the para position to the nitrogen atom already present.

Aniline black is rarely sold in the completed state, but is developed upon the fabric. It is used for dyeing cotton and in calico printing. It is less employed for wool, which, to take the dye successfully, is treated first with chlorine.

Most frequent use is made of potassium bichromate and copper salts; but since, in printing, the copper salts corrode the iron parts of the printing apparatus, these soluble salts of copper have been replaced by the insoluble sulphide of copper which, after being printed upon the fabric and in the presence of air and moisture, oxidizes to copper sulphate and then assists in the intended oxidation.

In printing a mixture of aniline hydrochloride, potassium chlorate and copper sulphide thickened with starch paste may be employed. The printed goods are hung in a room with moist air heated to about 30°. At first an oxidation of copper sulphide to sulphate takes place and then, through its action, the aniline salt becomes oxidized to aniline black. Vanadium salts have now largely replaced the copper salts.

For printing, it is important that the change from aniline to aniline black shall not take place in the paste containing the mixed ingredients; otherwise the paste would soon become useless, hence the more vigorous oxidizing agents such as chromic acid manganese peroxide cannot be used.

In dyeing aniline black a constant excess of acid must be present; but in printing this excess of mineral acid would injure the fabric and besides stimulate the formation of aniline black in the printing paste. In place of this acid it is often

customary to employ an excess of free aniline and partly replace the aniline hydrochloride with an alkali tartrate. Such a mixture will remain a long time inactive, forming no aniline black and only developing that color after it has been applied to the goods and been subjected to a certain degree of evaporation and consequent drying upon the fibre.

A disadvantage attending the dyeing and printing of aniline black is the tendency to turn to a greenish black on exposure to acid fumes; ever so slight an amount of such fumes as may be passed into the air from the burning of sulphur compounds contained in illuminating gas suffices to change the shade of goods thus exposed. The remedy is a more energetic oxidation during the printing, which seems to produce a black far less sensitive to these fumes.

In the dyeing of cotton a strong solution of aniline sulphate containing free acid and potassium bichromate is prepared and the cotton is immersed therein. As soon as the solution is heated, the developed aniline black attaches itself to the fibre. The aniline black thus produced is converted into the insoluble base by passing the goods through a bath containing sodium carbonate or suspended chalk.

CHAPTER XV

THE ALIZARIN DYESTUFFS

Turkey Red. This brilliant dye, on account of its fastness to light and to washing, has long been held in the highest esteem. Its use in dyeing was known to the Persians, Hindoos, and Egyptians. The presence of Turkey red in the wrappings of Egyptian mummies gives proof of its great antiquity.

The source of the dye was the root of the plant Rubia Tinctorum, more often called madder root. From the East the plant was first introduced into Italy under the name of Lizari or Alizari. Its cultivation began in Holland in the middle of the sixteenth century. Later the cultivation spread over many of the countries of middle and southern Europe and eventually to North and South America.

Madder is the form in which the dyestuff came into the trade. It is a fine dark brownish red powder made by grinding the madder roots, which have first been fermented in heaps and then dried. The growing root, however, exhibits no red color, but it contains a glucoside called ruberythric acid which by aid of fermentation or acids is broken up into a sugar and alizarin, the true dyestuff, according to the following equation:

$$\underset{\text{Ruberythric acid}}{C_{26}H_{28}O_{14}} + 2H_2O = 2C_6H_{12}O_6 + \underset{\text{Alizarin}}{C_{14}H_6O_2(OH)_2}$$

While alizarin is the chief constituent in madder of value to the dyer, it is accompanied by other coloring principles, purpurin and xanthin, besides resinous and gummy ingredients; these, during the elaborate operations of dyeing, were finally eliminated.

The agricultural production of the madder root and the manufacture of alizarin was suddenly threatened in 1868

with a rival artificial product from coal-tar through the discovery of two German chemists Graebe and Liebermann. They found that when alizarin was heated with zinc dust a new substance known as anthracene was formed. This clearly showed alizarin to be a derivative of anthracene, a long-known product of coal-tar distillation.

These chemists at once set about the task of reversing their newly discovered reaction in the hope of producing alizarin from coal-tar anthracene. The intermediate substance, a substance of quinone character, though it was not known to them, they called anthraquinone, and at the same time they regarded alizarin as dioxyanthraquinone. So much had their fusion of alizarin with zinc dust revealed to them. The recognition of alizarin as dioxyanthraquinone bore immediate fruit, for it enabled them to obtain alizarin by fusing dibromanthraquinone with potash.

This first success of a deliberate intention to prepare synthetically a dyestuff is one of the most illustrious technical attainments of modern times, and it is almost without parallel in the chemical technical consequences resulting from it.

It was next sought to substitute the cheaper sulphuric acid in place of the bromine, to form a disulphonic acid of anthraquinone which should in turn by fusion with caustic potash result in the formation of alizarin just as dibromanthraquinone had previously done.

The labors of Graebe and Liebermann, however, to produce alizarin from a sulphonic acid of anthraquinone were failures because they did not use a sufficiently high temperature to convert their primary material anthraquinone into its sulphonic acid. H. Caro, however, by employing sulphuric acid at a temperature of 200° C., succeeded in sulphonating his anthraquinone and obtaining a product which on fusion with potash yielded alizarin. Graebe and Liebermann together with Caro patented this process, while at almost the same date Perkin patented the process in England.

Alizarin. Pure alizarin is of an orange yellow color insoluble in water and found in the trade mixed with water in the form of a 20 per cent paste. It is never sold in the dry form for

the reason that it cannot be so finely divided again or so successfully suspended in the water of the dye-bath. Experience has shown that, though the alizarin in paste form is regarded as insoluble, is still dissolves in a slight but sufficient degree to fulfill its function as a dye while the dried alizarin has lost this power.

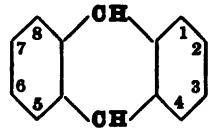
Alizarin by itself cannot communicate any color to a fabric. It is not a dye until it is brought in contact with a mordant, e.g., aluminum hydroxide, with which the fibres are charged. Its slight solubility enables it to combine with the mordant to form a red color. This combination of alizarin and mordant is termed a "lake." Subsequent operations profoundly modify the properties of this lake before the brilliancy of Turkey red is attained. The process necessary to accomplish this will be given later.

The technical difficulties in the way of the commercial manufacture of alizarin were great, but were soon overcome and the important process became one of the most prolific sources of revenue known to the color inuustry.

There were produced in Europe for each day of the year 1888, 60 tons of 10 per cent paste. Keen competition and the gradual perfecting of the methods lowered the price of alizarine from about $1.50 per pound for a 10 per cent paste in 1870 to 22 cents a pound for a 20 per cent paste in 1900.

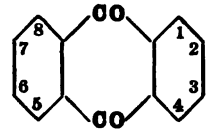
Alizarin and its Relation to Anthracine

Alizarin is not far removed in its constitution from that product of coal-tar known as anthracene. The formula of anthracene recalls that of naphthalene with the addition of another carbon ring. Its graphical formula is shown in the diagram below:



Anthracene

This hydrocarbon is found in that portion of the distillate of coal-tar boiling above 270°C. Under the influence of bichromate of potash and sulphuric acid, the central carbon atoms lose their hydrogen and take on oxygen, thus converting the anthracene into anthraquinone, whose formula reveals the change.

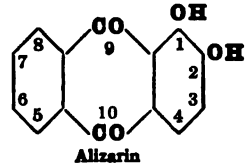


Anthraquinone

This substance is pale yellow, but it develops a more decided yellow to orange color when by further treatment it is converted into the hydroxyl derivative which is alizarin itself.

Of the many possible dihydroxy derivatives of anthraquinone, that one alone can produce colors with mordants which has the hydroxyl groups in the position 1:2 to the carbonyl group of anthraquinone. Thus alizarin alone possesses the power of dyeing prepared mordanted yarns or cloths.

Below is given the formula of alizarin:



Alizarin

To indicate the position of side groups in both anthraquinone and anthracene, use is made of a series of figures 1–8 as shown in the figure and the middle carbons are further numbered 9 and 10.

Alizarin crystallizes in the form of reddish brown needles which dissolve slightly in alcohol and scarcely at all in water. The crystals melt at 289°–290° C. and sublime at a higher temperature in beautiful long red needles. It dissolves with a violet color in a solution of caustic alkali. Carbon

dioxide causes a precipitation from this solution of the acid salt. Alizarin is oxydized to phthalic acid by nitric acid and is reduced to anthracene by heating with zinc dust.

Alizarine combines with various metallic hydroxides to form colored lakes and these are the insoluble dyes which remain fixed in the fibres of dyed fabrics. Of the various lakes, only four are much used in practical dyeing; those formed by the action of the hydrates of aluminum, chromium and iron and tin on alizarin. The aluminum lake is red, that of chromium brownish violet and that of iron blackish violet, that of tin rose.

For a long time the view was held that it was anthraquinone disulphonic acid which on fusion with potassium hydroxide produced alizarin. This view was later shown to be false, for only the monosulphonic acid of anthraquinone would give alizarin; the disulphonic acids, on fusion with potassium hydroxide furnished *iso*purpurin and *flavo*purpurin both of which are not di- but trioxyanthraquinones. As a matter of fact, this was known to a few technical chemists in 1871, but it was not generally known until it was published five years later by Perkin.

For the commercial manufacture of alizarin, the purest anthraquinone is used. The anthraquinone is prepared from anthracene by oxidation, using bichromate of potash and sulphuric acid. In practice a 50 per cent anthracene is employed and this by steam distillation is changed into a fine powder.

The oxidation is carried out in lead-lined vats arranged so that the mixture may be heated by direct steam. If only the purest anthracene is used and the oxidizing mixture is not too concentrated, the anthraquinone separates out as a soft gray powder. Washing frees it from all acid. The dried anthraquinone is then dissolved in concentrated sulphuric acid, and it is precipitated in a purer state by the addition of water. It is further purified by distillation with superheated steam.

To convert it into monosulphonic acid, it must be treated with fuming sulphuric acid containing 15 per cent of sulphuric anhydride at the lowest possible temperature. The β-mono-

sulphonic acid (the sulphonic group in the position No. 2 in the formula) seems to be the chief product, while the α-acid (having its sulphonic acid in the position No. 6) is formed in small quantities only.

The β-monosulphonic acid can be separated from some disulphonic acid unavoidably formed by the partial crystallization of the sodium salt of the former. By partial neutralization of the acid mixture, the anthraquinone monosulphonate of soda separates at first. The process is carried out so as to form as little of the disulphonic acid as possible.

In the old method of alizarin manufacture the oxidation process depended on the oxygen of the air, and consequently in order to give the air freest possible access to the fusion it had to be spread out in thin red layers in shallow vessels. But this method has been superseded for more than twenty years. Potassium chlorate is now used to furnish the necessary oxygen and the operation is carried on in closed vessels under pressure. The advantage of melting under pressure is the ease in regulating the temperature, especially when much water is present, while in open vessels a much greater concentration was necessary to reach the required temperature.

One part of anthraquinone monosulphonate of soda and three parts of sodium hydroxide are placed with potassium chlorate and a certain amount of water in a horizontal cylindrical iron kettle provided with a stirrer. It is then stirred and heated for a long time to 180–200° C.

The fusion is then dissolved in water and the alizarin precipitated with hydrochloric acid, which decomposes the soluble sodium compound, setting free the insoluble alizarin to settle as a precipitate.

Alizarin appears in commerce as a yellow paste containing 80 per cent of water. The reason for selling it as a paste is that it forms a powder when dried which is difficult to distribute in water in a sufficiently fine and homogeneous condition for dyeing operations. But when shipped to India, it is in the form of a dry powder prepared from a paste previously mixed with starch. When this powder thus prepared is placed in water the swelling of the starch granules separates

the particles of alizarin, forming a thin paste suitable for the dyer.

Russian dyers, however, purchase alizarin in the form of a dry powder, which they dissolve in caustic soda and then precipitate in the dye bath itself with hydrochloric acid. This process is said to give more intense dyeings than those obtained with alizarin in the paste form.

A distinction is made between a bluish and a yellowish alizarin. This does not mean that a pure alizarin varies in color, but simply that those varieties of alizarin found in the market are somewhat impure, the bluish being the purer of the two and the yellowish contaminated with both of the trioxyanthraquinones, *iso*purpurin and *flavo*purpurin.

Application of Alizarin in Dyeing

Immemorial usage in the production of Turkey red with madder brought the art to a high state of perfection by the aid of empirical processes most elaborate and tedious. The success of this highly prized color involved, according to J. J. Hummel, in the emulsion process no less than fourteen different operations. Beautiful results were secured by its use. The yarn was first boiled in a solution of sodium carbonate and dried, the worked in an emulsion of oil, dung, and sodium carbonate, steeped in water and in sodium carbonate, sumached, mordanted with aluminum hydroxide, dyed with 10 per cent alizarin sumach and blood, cleared with sodium carbonate, finally clearing with soap and stannous chloride. To finish these processes required about three weeks, but a genuine Turkey red was produced, brilliant and durable.

The substance which remained upon the fibre and gave the red color was not a simple lake formed by the union of the acid alizarin and the basic aluminum hydroxide, but a more complex substance which contains besides these two elements two other inorganic bases, viz.: lime and stannic oxide and in addition tannic acid, fatty acids and sometimes phosphoric and arsenic acids which with the alizarin constitute the acid portion of this very complex lake. Turkey red, therefore,

strikingly illustrates the rule that a color is stable in proportion to the number of different constituents of the lake.

In dyeing Turkey red, the only mordant base which is directly applied is a salt of aluminum. The lime and stannic oxide contained in the final actual lake are introduced during the different operations of dyeing and clearing.

Yarn is mordanted by immersing in a solution of alum or aluminum sulphate and then in a bath of sodium carbonate or chalk. The same mordant answers for printing calico or other cotton fabrics. Colored designs on a white ground are secured by printing the mordant on the places which are later to appear colored. A special mordant for this purpose is prepared by adding a solution of alum to a solution of lead acetate insufficient to cause a total or complete double decomposition with the addition of some sodium carbonate. The solution contains both basic acetate and basic sulphate of aluminum. Aluminum acetate alone gives less desirable results, for it makes the goods impervious to water and difficult to wet out. Starch is used to thicken the mordant in printing.

The aluminum hydroxide is precipitated from that portion of the solution which has actually penetrated the fibre by the following operations; these leave the hydroxide in a granular and not in a gelatinous condition.

The goods are hung in a large room kept at a temperature of 32–40° C. with careful regulation of the amount of moisture present. Here it remains until by the loss of a considerable portion of the acetic acid, the salts of aluminum become more basic and at the same time nearly insoluble.

The next operation, called dunging, consists in passing the goods through a hot bath which contains cow's (or pig's) dung and chalk. The sulphuric acid and what remains of the acetic acid is removed by the chalk, while by mechanical action principally, the dung prevents any detached parts of the mordant from contaminating the white parts of the fabric. The pieces after thorough washing are passed into the dye bath containing alizarin which beginning at a low temperature finally rises to a boil.

Analysis of materials dyed with madder, a natural mixture of alizarin and purpurin, seems to show that the red contains alumina and lime in the ratio of two molecules of Al_2O_3 to three molecules of CaO. Investigations of Liechti and Suida show the most probable formula of the usual alizarin lake to be

$$Al_2O_3CaO(C_{14}H_6O_3)_3 \cdot H_2O$$

This ratio of the lime to the alumina is disturbed in the later process of soaping which removes some of the lime. The goods contain lime taken up from the chloride of lime used in a previous bleaching process but more is taken from the calcareous water used in making up the dyebath.

Rosenstiehl states that the presence of lime in the water is a necessity. The alizarin-lime lake, though insoluble in pure water, easily dissolves in water containing carbonic acid; and as natural waters usually contain calcium bicarbonate as well as free carbonic acid, a considerable amount of the alizarin is dissolved as a lime lake and this is then taken up as such by the aluminum hydroxide in the fibre. But the final high temperature of the dye bath causes the evolution of carbon dioxide and the consequent precipitation of lime lake, which accumulates on the bottom of the vat and thus entails a loss of alizarin. To counteract this evil Rosenstiehl recommends adding calcium acetate to the dye bath, or if the water contains much lime, acetic acid alone. The bath is maintained slightly acid at first. The alizarin dissolving in the calcium acetate gradually decomposes it on a sufficient increase of temperature. Acetic acid is thus set free and the alizarin-lime lake which is formed and also free alizarin unite with the aluminum hydroxide in the fibre.

At this stage of the process the red has a dull appearance and it has to pass through the clearing process to attain its full brilliancy. Boiling in a solution of soap and stannous chloride follows. The action of the latter, though complicated, accomplishes in part the removal of some of the sodium from the soap and forms stannous hydrate. The soap, thus rendered more neutral, more easily gives up fatty acid to the color

lake. This is proved by the taking up of an appreciable amount of fatty acid during the process. The stannous hydrate works on the brown impurities fixed on the fabric with the alizarin. It reduces and thereby decolorizes them. At the same time, it is itself gradually oxidized to stannic hydrate and this combines with a portion of the alizarin to form an orange lake and thus the entire red color is brightened.

Another method of securing the same brightening effect is to pass the dyed pieces through a moderately warm bath of a soluble stannous salt, nitro chloride of tin. This is formed by the addition of stannous chloride to an equal weight of nitric acid.

The fastness of alizarin red depends upon the presence of fatty acids or oxidized fatty acids. The soaping operation does not furnish sufficient fatty acid and the other operations are required to thoroughly saturate the fibre with this necessary substance. Turkey red, the most permanent color obtained with alizarin, contains the largest amount of fatty acids.

The oil upon which the dyers used to depend to furnish this fatty acid in the old method was called "huile tournante" or gallipoli. It is a variety of olive oil which by partial decomposition contains free oleic acid and this forms an emulsion when used with alkaline carbonates.

The yarn or fabric was passed through an emulsion of this kind and then by exposure to air a part of the oil was oxidized to compounds insoluble in alkaline carbonates. This process consumed much time and was very tedious.

Rancid gallipoli is no longer used, or at least infrequently. The so-called "Turkey red" oil produces the same result more efficiently and more rapidly. It is prepared from castor oil by the action of sulphuric acid below 40° C. and washing with brine or sodium sulphate solution to remove free acid and then neutralizing with ammonia or sodium carbonate.

Though the composition of the product is somewhat uncertain, it is regarded as the alkali salt of ricinoleo-sulphuric acid $C_{17}H_{32}(HSO_3 \cdot O)COOH$. The process of oiling may be carried out before or after mordanting with aluminum hydroxide or even after dyeing if the process is subsequently assisted

by steaming. In some instances the Turkey red oil is added to the dye bath itself.

Tannin in some form, as sumach or catechu, is added to the dye bath, for by uniting with part of the aluminum hydroxide it forms fuller shades. Glue may be added to form insoluble compounds with the tannic acid and thus protect parts of the design which are to remain white. On heating the dye bath, the aluminum hydroxide on the fibre decomposes the finely divided compound of tannic acid and glue and it becomes saturated with tannic acid.

It is absolutely necessary in the production of fine shades from alizarine that there be not the slightest trace of iron present, which changes fine red or pink to a dull red or even brown. Special attention is therefore required to guard against traces of iron, but as the color in printing is in constant contact with the steel scrapers (called the "doctors") of the printing rolls, traces of iron cannot be prevented from being taken up by the color, but the presence of iron even is harmless if it can be prevented from entering the alizarin lake in the ferric state, and this can be effected in several ways.

Addition of stannous chloride or stannous hydrate reduces all the iron to the ferrous state. Arsenious acid, by combining with the ferric iron to form an insoluble salt, renders it harmless, for this salt is not decomposable by alizarin. If sulphocyanide is added to the color, the iron, oxidized to the ferric state by nitrate of aluminum, forms a ferric sulphocyanide.

Alizarin Violet is produced on cotton by a process very similar to that used in Turkey red dyeing. The blue shade of alizarin is used, the yellow shade cannot be employed for this purpose, because the anthrapurpurin present in the latter gives grayish violet effects while the flavopurpurin also produces a reddish violet.

Ferrous acetate is the mordant used. In the dyeing chamber, it is decomposed into ferric hydrate and acetic acid. The goods are then treated with cow's dung and chalk, after which washing and dyeing with alizarine follows. Sodium arsenite is often used in the dye bath to produce faster and brighter shades. Part of the ferric iron in the bath is reduced to ferrous

iron and thus a compound lake of ferric and ferrous oxides results. The reduced ferrous oxide is supposed to play the part in violet that lime does in the red. In the color arsenious acid is also found.

Brown. Alizarin red may be toned brown by the admixture of Prussian blue. Fine shades of brown may also be secured by a mixture of iron and aluminum mordants.

Wool. Alizarin is used to advantage in dyeing wool on which colors similar to those on cotton are produced which are fast to milling and light. The wool is mordanted by boiling it with alum and cream of tartar. To obtain bright colors, it is necessary to use acid calcium acetate or acetic acid, and furthermore it is necessary to dye first cold, gradually and slowly heating the bath to a final boiling temperature.

The colors obtained with tin as a mordant are not affected by light, but they become dull on milling with soap.

Silk. Alizarin and related dyes may be applied to silk which has been charged with various metallic mordants. Brightening is accomplished by boiling in a soap bath. Full and fast colors are produced, but they are applied only in those cases where fastness is a necessity.

Recovery of Alizarin from the waste of the dye bath. On passing goods dyed with alizarin through the chalk bath after steaming, the surplus alizarin detaches itself and falls to the bottom of the vat in the form of a lake or lakes, together with other impurities, forming a mud. To recover the alizarin, the mud is treated with dilute hydrochloric acid,which separates the alizarin in insoluble form; this is collected and washed. Then it is dissolved in dilute soda filtered and reprecipitated with hydrochloric acid.

If iron should be present in the color, warm sulphuric acid will dissolve it, leaving pure alizarin behind.

Reactions of Alizarin on Textile Fabrics. Boiling solutions of caustic alkalies moderately concentrated do not remove any of the color from the dyed fabrics nor do diluted acids effect a change. Concentrated acids act by partially or wholly removing the metallic base from the color lakes. The different alizarin colors possess varying powers of resistance against

acids; thus the violet is more easily decomposed than ordinary red, while the greatest resistance is offered by Turkey red.

Cotton fabrics are completely dissolved together with the dye itself in concentrated sulphuric acid, but on diluting with water the dye is separated as an insoluble flocculent precipitate which is then caught on a filter, washed and dried. It may then be sublimed or recognized by the violet color it imparts to alkaline solutions.

Powerful oxidizing agents like nitric acid or ferric chloride destroy alizarin.

Chloride of lime in dilute solution has no effect upon Turkey red, but the ordinary alizarin red is gradually destroyed. The simultaneous action of chloride of lime and an acid will destroy even Turkey red.

Useful application is made of this property in producing white designs upon a Turkey red ground. The red fabric is printed with tartaric acid and then passed through a solution of chloride of lime. On the spots printed with the acid, the color is bleached by the liberated chlorine and at the same time the excess of tartaric acid dissolves the alumina.

Alizarin is not affected by potassium bichromate, but it is destroyed by free chromic acid. White designs may therefore be produced on red by passing the fabric through a solution of potassium bichromate and then printing with tartaric acid, which, by liberating chromic acid, bleaches the color.

Nitrous fumes change alizarin red to alizarin orange.

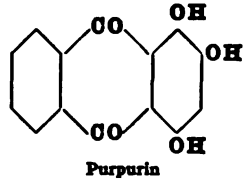
Though the alizarin colors are not affected by light and air, they are temporarily changed by heat to a brownish red. Exposure to air at the ordinary temperature almost completely restores the color. This change is supposed to depend upon the loss of water of hydration from the red color by the action of the heat and the regaining of it again from cool moist air.

Trioxyanthraquinone

Purpurin. In the madder dyestuff prepared from the madder root, a second coloring matter named purpurin was always found accompanying the alizarin. When madder

was used in dyeing, the purpurin showed the property of uniting with mordants and forming a shade of red which modified to some degree the red shade of alizarin itself.

Purpurin is a derivative of anthraquinone and differs from alizarin in the possession of one more oxygen atom. This extra oxygen atom has a definite position in the molecule as may be seen from the following formula:



Purpurin

Purpurin possesses the property not shared by alizarin of dissolving in a solution of aluminum sulphate, and this property is made use of in separating and estimating the amount of purpurin in a sample of commercial alizarin. It is only necessary to boil the sample in a solution of aluminum sulphate; the purpurin dissolves, leaving behind the insoluble alizarin, which is filtered off. By adding an acid the purpurin is precipitated, collected on a filter and weighed.

Small amounts of alizarin may be detected in purpurin by dissolving the sample in a solution of sodium hydroxide, and exposing to light. The purpurin is in time competely destroyed, while the sodium alizarate remains unaffected. The unchanged soluble sodium alizarate will on the addition of sulphuric acid form alizarin. This alizarin may be separated from the liquid by shaking with ether, evaporating to dryness and the residue tested in the ordinary way for alizarin.

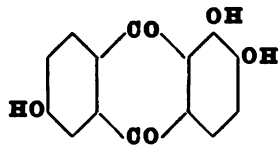
Although the alkaline solution of purpurin quickly fades on exposure to light, yet the combination of purpurin and an aluminum mordant produces a beautiful scarlet which is fast to light.

Purpurin may be made artificially from alizarin by oxidizing it by means of sulphuric acid and manganese dioxide, or arsenic acid or by fusing alizarin sulphonic acid (the so-called alizarin purpurin sulphonic acid) with potassium hydroxide.

The red produced upon cloth charged with an aluminum mordant is much yellower than that produced by alizarin under the same circumstances.

Purpurin produces upon cloth mordanted with chromium hydroxide a reddish brown. On account of its high price and its inferior fastness to light, it enjoys but a limited technical use. Flavopurpurin is isomeric with purpurin and the only difference in its constitution is the change of one oxygen atom from position 4 in purpurin to 6 in flavopurpurin. This change of position in the oxygen atom induces a change in the shade of the dye with an alum mordant from scarlet to a yellower red than purpurin.

The structure of flavopurpurin is shown as follows:



Flavopurpurin

Flavopurpurin consists of a brownish yellow paste which will not dissolve in cold water and only with difficulty in boiling water. The dry substance dissolves easily in alcohol and crystallizes from its solution in golden yellow needles which melt at over 336° C.

It dissolves easily in sodium hydroxide, forming a purple solution of the sodium salt, but the ammoniacal solution is brown in color. The reddish brown color of the dye dissolved in concentrated sulphuric acid is changed on adding sufficient water to the orange yellow color of the dyestuff, as it is precipitated in an insoluble condition.

Cotton is dyed with an alum mordant to a red which is yellower than *iso*purpurin. It is used especially for cotton printing. In combination with alizarin it is employed for producing the most common shades of Turkey red. Flavopurpurin sometimes replaces madder for fast dyeing upon wool. Together with alizarin and alizarin orange it was used for dyeing the leggings of the cavalry in the Austrian army.

The permanent character of the dye is shown by its withstanding unchanged the test of a 30-day exposure to July and August weather. Dyed wool suffers no change by the action of sulphurous acid of 4½ Bé.

Flavopurpurin is a hydroxyl derivative of alizarin and it contains the third hydroxyl group in the second benzene ring.

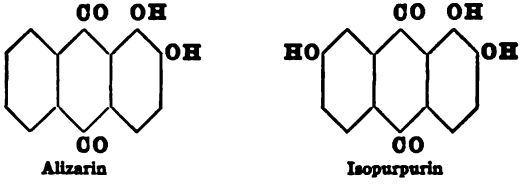
It is prepared by melting α-anthraquinone disulpho acid with sodium hydroxide and potassium chlorate. By this process two dioxyanthraquinones anthraflavic acid and *iso*-anthraflavic acid are formed and they often occur in the commercial product. They are valueless for coloring purposes and only occasion loss of material.

Flavopurpurin is especially suited for printing on cotton goods, since it combines with mordants more readily than alizarin and *iso*purpurin is developed only by a gentle steaming.

Isopurpurin. This dyestuff was originally found to accompany the alizarin obtained from the madder root and in consequence the colors produced from alizarin were modified by its presence.

It is now produced from coal-tar anthracene in a manner analogous to that for alizarin.

*Iso*purpurin is a trihydroxy derivative of anthraquinone or a monoxy derivative of alizarin. It has the same empirical formula as purpurin and flavopurpurin and only differs from these so far as structure of its molecule in the position of one oxygen atom. By comparison of the formulas of alizarin and purpurin below we see their close resemblance:



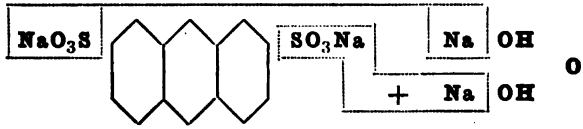
Alizarin Isopurpurin

*Iso*purpurin is formed by melting β-anthraquinone disulpho acid with sodium hydroxide and potassium chlorate. *Iso*anthroflavic acid is formed as an intermediate product.

It forms a brownish red paste as a commercial article, but orange-colored needles when the dry substance is crystallized from hot alcohol. Cold water does not dissolve it and hot water only with difficulty. It does not dissolve in benzene, but is easily dissolved in alcohol and the needle-shaped crystals obtained from its solution melt at over 330° C.

In a solution of sodium hydroxide it dissolves to form a bluish violet color; in an ammoniacal solution the color is reddish violet. Strong sulphuric acid dissolves it with a brown color, but dilution with water causes an orange yellow insoluble precipitate of the unchanged dyestuff.

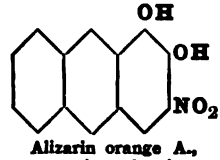
Cotton mordanted with alum is dyed a scarlet red.



β-Anthraquinone disulpho acid

Alizarin Orange A. This orange dye is a brownish yellow paste which is prepared from alizarin by simply treating it with nitric acid of a strength 30–40° Bé. The insoluble alizarin is suspended in ligroin or nitrobenzol or glacial acetic acid to enable the nitric acid to act upon it.

The action of the nitric acid consists in implanting a nitro group in position 3 of the first benzene ring of the alizarin molecule as shown by the formula below:



Alizarin orange A., or β-nitro alizarin

If the alizarin orange be dried, it forms orange yellow needles which will dissolve in benzene or glacial acetic acid and melt at 244° C.

The dyestuff dissolves in a solution of sodium hydroxide, forming a rosaniline color. If zinc dust is added to this solu-

tion the color changes to blue, then later to a yellowish brown. However, on exposure to the air this latter color goes back again to blue.

Strong sulphuric acid dissolves it with a yellowish brown color which, on the addition of water, deposits a bright yellow precipitate.

The influence of the single nitro group is seen when this dye is employed with the various mordants in comparison with alizarin itself.

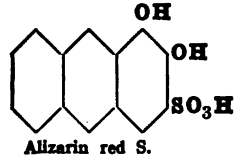
Pure alizarin with an alum mordant on cotton yields a red, while this dye yields an orange; alizarin with an iron mordant produces a violet and with a chromium mordant brownish, while alizarin orange A with an iron mordant a reddish violet and with chromium a reddish brown.

Alizarin orange A also serves as a starting point in the manufacture of alizarin blue.

Alizarin Red S. Alizarin. If alizarin which is insoluble in water is treated with sulphuric acid, a sulpho acid is formed and the resulting product will dissolve in water.

To effect this, 1 part of alizarin is heated to 100°–150° C. with 3 parts of concentrated sulphuric acid containing 20 per cent of the anhydride. The process is completed when a sample dissolves completely in water. The product is dissolved in water and the excess of sulphuric acid is precipitated by milk of lime or barium hydrate. The filtrate obtained is made neutral and then evaporated.

Alizarin monosulphonic acid is the product from the acid and with the position of the sulpho group corresponds to that in the formula:



Alizarin red S.

This free sulpho acid is soluble in water. The commercial product is the sodium salt $C_{14}H_5O_2(OH)_2SO_3Na$; it dissolves in water with a yellow color. When an excess of sodium

hydroxide is present the other two hydrogen atoms are replaced by sodium, forming a very soluble salt that dissolves in water with an intense violet color.

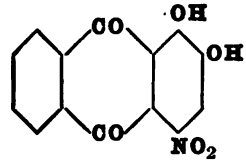
The addition of hydrochloric acid to the commercial product changes it to bright yellow. Concentrated sulphuric acid gives a yellowish red solution which turns bright yellow on adding water. Sodium hydroxide turns the solution violet.

Though the dye is soluble in water, it cannot be used to dye wool directly, and to obtain a red on wool it is necessary to use an alum mordant. A good scarlet results from one bath with alizarin red S alum and oxalic acid. This dye possesses the advantage of being used upon wool, for which alizarin itself is poorly adapted.

The application of sulphuric acid is not limited to making a soluble sulpho acid of alizarin, but it is used in the same manner upon several other hydroxy derivatives of alizarin.

Alizarin Red 3W.S. By treating flavopurpurin with sulphuric acid in a manner similar to that for alizarin red S., a soluble sulpho acid is formed containing one sulpho group in position 3 of the molecule.

Alizarin Garnet R. Alizarin Cardinal. When nitric acid acts upon alizarin under suitable conditions, a nitro alizarin is formed by the fixation of one nitro group in position 4 in the molecule.



α-Nitroalizarin

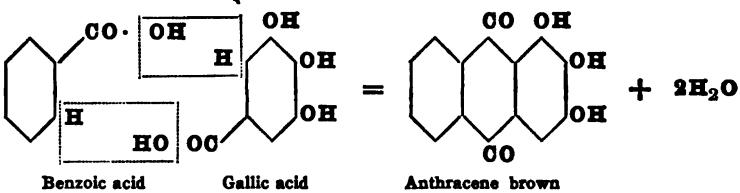
This product is called α-nitro-alizarin, and though without value as a dye, it is on reduction converted into an amino alizarin, which is the dye alizarin Garnet R. The conversion of α-nitro-alizarin into the amino compound is effected by the alkali sulphides.

The dyestuff will not dissolve in water and it is sold as a carmine red to reddish brown paste. Alcohol dissolves it

with a carmine red color. Hydrochloric acid turns the paste brown. Sodium hydroxide produces a carmine red solution. The brown solution in strong sulphuric acid yields a carmine red precipitate with addition of water.

Cotton mordanted with alum is dyed a bluish red. It is also used for calico and for modifying the shades of alizarin. Wool is also dyed with it.

Alizarin Brown is a derivative of alizarin, which contains one additional oxygen atom, and it thus becomes a trioxy derivative of anthraquinone. Though it is a derivative of alizarin, it is not formed from it. Two substances very unlike the final product are brought together and caused to unite under the influence of sulphuric acid, which abstracts water during the reaction. One method employs gallic acid, benzoic acid and sulphuric acid, and the reaction may be represented thus:



Benzoic acid — Gallic acid — Anthracene brown or anthragallol

By comparison of the formulas, anthracene brown will be found to be isomeric with purpurin, flavopurpurin and *iso*purpurin.

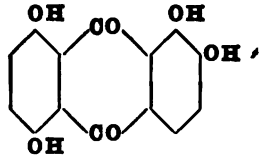
Anthracene brown may also be prepared by the action of anhydrous zinc chloride upon phthalic anhydride and gallic acid. The zinc chloride in this instance serves the same purpose as the sulphuric acid in the other method of manufacture, that is, abstracting the elements of water.

The dyestuff is sold as a dark brown paste which does not dissolve in water, but does dissolve in alcohol with a yellow color. Hydrochloric acid causes no change. Sodium hydroxide produces a greenish blue color. Strong sulphuric acid dissolves it with a brownish red color, but this solution deposits a brown precipitate when water is added.

Cotton which has been mordanted with chromium salts is dyed a fast brown. It is also employed in printing upon cotton. It is also used upon wool with the aid of a chromium mordant.

Tetraoxyanthraquinones

Alizarin Bordeaux B: If ordinary alizarin with its two hydroxyl groups be oxidized with strong fuming sulphuric acid containing 80 per cent of the anhydride and a temperature of 30° C. is maintained for three or four days, a change occurs and two oxygen atoms are added in certain definite positions in the molecule and thus two additional hydroxyls are added. The product is consequently a tetraoxyanthraquinone and the new hydroxyls are to be found in positions 5 and 8 in the molecule as shown below:



Alizarin Bordeaux B. Tetraoxyanthraquinone

The brownish red paste which is the commercial form of this dye does not dissolve in water, but it goes into solution in alcohol with a brownish orange color.

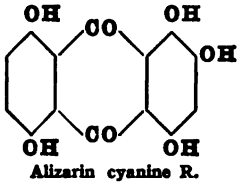
Sodium hydroxide yields a reddish violet solution. The solution in concentrated sulphuric acid is bluish violet, which on dilution with water yields a brownish red precipitate.

This is a mordant dye similar to alizarin, but it produces with the various mordants much bluer shades than alizarin. It produces on cotton with an alum mordant by the Turkey-red process bright and fast shades of a bluish claret. Violet blue shades are produced by a chromium mordant. Wool receives bright bluish shades with a chromium mordant.

Pentaoxyanthraquinones

Alizarin Cyanine R. This dye is produced directly from alizarin Bordeaux B. just mentioned, by oxidizing it with manganese dioxide and sulphuric acid. One oxygen atom is

added which gives rise to an extra hydroxyl group in position 4 in the first ring. This additional hydroxyl group in this position has the effect of producing bluer shades than alizarin Bordeaux B. with its three hydroxyl groups.



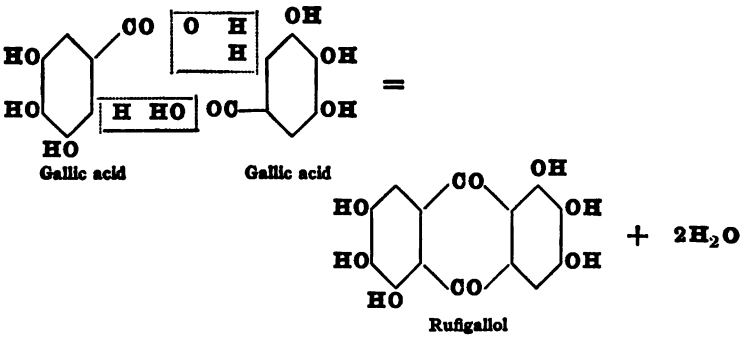
Alizarin cyanine R.

The dye is sold as a dark brown paste which water does not dissolve. In glacial acetic acid it dissolves with a yellowish red color possessing a greenish fluorescence. Sodium hydroxide and sulphuric acid dissolve it to form a blue solution. In concentrated sulphuric acid it dissolves with a blue color and a reddish fluorescence; this solution on dilution with water lets fall a dark brown precipitate.

Wool mordanted with alum is dyed violet and with a chromium mordant blue. The color is fast to the action of acids, alkalies and light.

Hexaoxyanthraquinones

Rufigallol. This derivative of alizarin, with its six hydroxyl groups, is not an oxidation product of alizarin. It is formed from two molecules of gallic acid, each already possessing three hydroxyl groups. They are caused to combine into the alizarin derivative by the influence of sulphuric acid.



Gallic acid Gallic acid

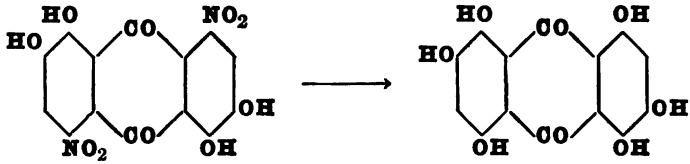
Rufigallol

Rufigallol is a brownish powder which is insoluble in water. If hydrochloric acid is added no change is effected. Sodium hydroxide dissolves the paste to a blue solution which changes rapidly on exposure to the air. It dissolves with a red color in strong sulphuric acid.

Wool by the aid of a chromium mordant is colored brown.

Anthracene Blue W. R. It is of interest to note that anthracene blue W.R. is isomeric with rufigallol. Six hydroxyl groups are found in each—three in each benzene ring. Difference of position alone of these groups makes a brown dye of one and a blue dye of the other.

The starting point for this dyestuff is 1:5-dinitroanthraquinone



Dinitroanthroquinone — Anthracene blue W.R.

which by means of fuming sulphuric acid containing 40 per cent anhydride is converted into a product that needs only to be heated with dilute sulphuric acid to convert it into the blue dye.

The commercial dyestuff is a dark brown paste which water does not dissolve, though alcohol dissolves it with a reddish color and a yellow fluorescence. Sodium hydroxide forms a blue solution. Concentrated sulphuric acid dissolves it with a violet blue color and a brownish red fluorescence.

Wool with an alum mordant is dyed violet; but with a chromium mordant blue. It is used in cotton printing with alum and chromium mordants.

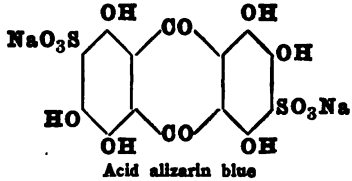
On account of the fastness of its dyeings, anthracene blue W.R. is especially suited to produce blue shades upon cloths used for military uniforms which must undergo exposure to all kinds of weather.

Acid Alizarin Blue B.B., G.R. By comparing the formula of this dyestuff with that of anthracene blue W.R. a dif-

ference of two sulpho acid groups will be observed. They are located in positions 3 and 7. Under their influence the dyestuff is soluble in water.

The dyestuff itself is the sodium salt of the disulpho acid of anthracene blue W.R. but it is not prepared from this dye.

The initial substance used in its preparation is diamino-anthrachryson disulpho acid. This by boiling with alkalies loses its two amino groups while retaining its two sulpho acid groups, which form salts with alkali present. Its structure is shown below:



Acid alizarin blue B.B. and G.R.

The dye appears as either a dark or bright red crystalline powder which dissolves with a red color in water. However, it will not dissolve in alcohol.

Hydrochloric acid causes a reddish violet precipitate to fall. Sodium hydroxide turns the solution a violet blue, and if an excess be added a precipitate falls. In concentrated sulphuric acid the color is bluish and on dilution the color turns to that of the simple aqueous solution.

Wool in an acid bath is colored blue with a reddish cast. By subsequent treatment with chromium fluoride a purer blue is produced. It is unaffected by acids and alkalies and it is also fast to milling.

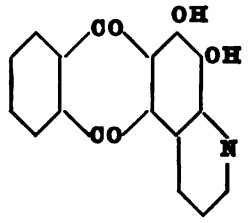
Four weeks' exposure to August and September weather had no effect upon its fastness.

Alizarin Blue R. This valuable blue dye is a direct derivative of alizarin, but differs from the alizarin previously considered by containing an additional ring, and in this ring is found a nitrogen atom. It partakes in consequence of the character of quinoline. The chemical name of the dye is dioxy-anthraquinone quinoline.

For its preparation, alizarin is treated in such a manner

as to produce β-nitroalizarin; thus the necessary nitrogen atom for the new ring is introduced. Now by the further treatment of this product with glycerin and sulphuric acid in the presecne of nitrobenzene and aniline the dyestuff is formed. The three carbon atoms of the glycerin molecule furnish the carbon atoms for the new quinoline ring.

The new ring and the original alizarin molecule are easily seen in the following formula:



Alizarin blue R.

This synthesis, first employed for making this dyestuff, was carefully studied by Graebe, who concluded the structure to be represented by the accompanying formula. The belief that a quinoline compound was actually formed here was most beautifully confirmed by Skraup, who prepared pure quinoline itself by heating together aniline glycerin sulphuric acid and nitrobenzol.

The method now employed for producing alizarin blue is similar to the synthesis of quinoline, for it is now manufactured by heating nitroalizarin, aminoalizarin with glycerin and sulphuric acid to 105° C. When the heated mass is poured into water the alizarin blue is precipitated and thoroughly washed from the persistently adhering sulphuric acid. Almost quantitative yields of the dye are obtained.

Alizarin Blue S. This dye differs from alizarin blue in being soluble in water. It is prepared directly from alizarin blue by treatment with sodium bisulphite. In appearance it is chocolate brown powder that dissolves easily in water with a yellowish brown color. In alcohol it does not dissolve. Hydrochloric acid turns to a reddish yellow while sodium hydroxide yields a bluish violet solution. In strong sulphuric

acid it dissolves with a dark yellow color; addition of water produces a brown precipitate.

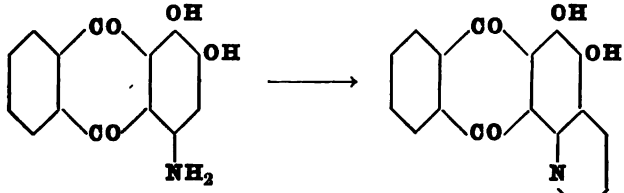
When a solution of this dye is heated over 70°C., it dissociates from its sodium bisulphite combination and the insoluble alizarin blue separates. Its use in printing depends upon this property, for by printing the dye upon cotton mordanted with chromium and then steaming the decomposed salt forms with the mordant a lake of a blue color.

Strong acids and alkalies and even alkali carbonate decompose the soluble combination of sodium bisulphite with the dyestuff.

Alizarin Blue S has been employed as a substitute for indigo, but it is inferior to it in its fastness to light.

Alizarin Green S. A change in the position of one nitrogen atom in the molecule of alizarin blue S suffices to change the dye from blue to green, as it is used with a chromium mordant upon cotton. This change produces alizarin green S.

The new position of the nitrogen atom is secured by employing α-aminoalizarin or alizarin garnet R as the starting point. In this substance the nitrogen is already fixed in the desired position and by heating it with glycerin, sulphuric acid and nitrobenzol, the new ring is completed in the form shown:

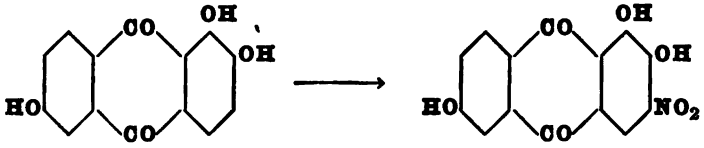


α-Aminoalizarin — Alizarin green S.

The dye is a black paste which is soluble in cold water on account of treatment with sodium bisulphite. From its solution, the alizarin green will separate under the influence of heat or of hydrochloric acid. Sodium hydroxide turns the solution violet. It forms a dark blue solution in strong sulphuric acid from which dilution with water forms a dark blue precipitate.

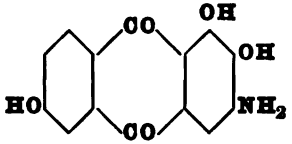
Wool mordanted with chromium salts is dyed a fast bluish green. It is also employed in calico printing.

Alizarin Black P. Few derivatives of alizarin are capable of yielding black dyes. The blue dyes, however, when used of sufficient strength, produce shades which are almost black. In the present instance flavopurpurin must first be nitrated as a starting point.



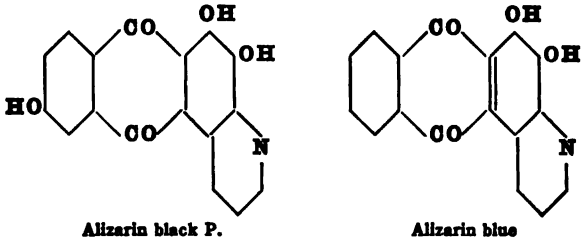
Flavopurpurin — β-Nitroflavopurpurin

The nitro compound may then be reduced to the amino compound which, upon being subjected to action of glycerin, sulphuric acid, nitrobenzene and aniline is enriched by the



β-Aminoflavopurpurin

addition of a nitrogen-bearing ring. Thus a quinoline derivative is formed, the structure of which is seen to be as follows:



Alizarin black P. — Alizarin blue

By comparison of the annexed formula of alizarin blue, it will be seen that with the development of a hydroxyl group in position 6 of this dye a change from blue to black would result.

Alizarin black P is a greenish black paste which water does not dissolve, though alcohol dissolves it with difficulty. Hyrochloric acid turns the paste to a brownish color. Sodium hydroxide dissolves the paste, forming a dirty green solution. A dirty reddish brown solution is effected by strong sulphuric acid; addition of water turns the solution yellowish brown and then as the diluted solution cools a brown precipitate falls.

Wool mordanted with chromium is dyed violet gray to black according to the amount of dyestuff employed.

CHAPTER XVI

INDIGO

Among all the coloring matters employed by man, indigo may fairly claim to be the oldest and most valuable. Blue ribbons taken from the wrappings of mummies that were 5000 years old have been proved to contain indigo as the coloring matter.

Its value and fastness are such that old army uniforms containing three per cent by weight of the blue dye have been treated with reducing agents to dissolve and recover this valuable and durable color.

Indigo is now obtained from the indigo plants (Indigofera tinctoria chiefly) and synthetically from the coal-tar products. No more striking example of the attainments of modern synthetic chemistry could be shown than the successful competition of the synthetic product resulting from less than a score of years of arduous research with the natural product from the plant, the result of 50 centuries of culture and manufacture.

The alarm now felt by the indigo planters of India, whence comes to-day most of the natural indigo, as they see a shrinkage of thousands of acres in area formerly devoted to indigo culture, is so great that the Indian Government has become aroused upon the question and has appointed experts to find out how the indigo industry may be saved from ruin by the introduction of improved methods of culture and manufacture and the production of a pure and honest product.

The same fate now threatens the rich Indian planters which overtook the European growers of madder, when in 1868 began the gradual but sure extinction of the culture of madder by the discovery of synthetic alizarin from coal-tar; the

same alizarin that was more laboriously extracted from the root of the madder plant.

There is something of a just though none the less tragic retribution falling to-day upon the Indian planters. From time immemorial they have enjoyed the princely incomes of their great estates, feeling secure in their position and wholly indifferent to improved methods and with the Oriental willingness to rather increase their profits by scandalous adulteration. It remains to be seen, now that the peril is appreciated, whether the culture may be so economically carried on as to retrieve their position against the purer synthetical product now so well intrenched in the markets of the world. The issue is extremely interesting and also extremely doubtful.

Natural Indigo: Vegetable Indigo

Indigo does not occur in the plant as a blue substance, but as a chemical constituent of a more complex colorless compound in the juice of the leaves of the plant. This compound is known as indican, and is dissolved from the leaves of the plants as they are steeped and fermented under water in large steeping vats. The soluble indican passes off in solution as the water is drained away from the plants into other vats where the liquid is agitated for several hours; sometimes by coolies who stand waist deep in the liquid, beating it into a froth with bamboo poles, or sometimes by paddlewheel machines. The purpose of this agitation is to expose the liquid to the oxygen of the air. Meanwhile the soluble and colorless indican is decomposing into a sugar and indigo white which takes up oxygen from the air and is converted into insoluble indigo blue. This can now be separated by filtration from the liquid.

Formerly this was supposed to be the way the indigo was produced, but of late years much difference of opinion has arisen over the chemical explanation of the process; one view being that indican breaks up into glucose and indoxyl which in turn oxidizes into indigo.

Indigo was introduced into Europe in the sixteenth century; but for a great many years its extensive use was success-

fully opposed by the cultivators of woad (Isatis tinctoria) a plant producing an inferior variety of indigo blue dye. These woad growers industriously circulated the report that indigo was not only an inferior dye, but also a corrosive and pernicious drug. Fear of the ruin of the woad business from the new competing dye was the real motive of their false reports.

So much feeling was aroused that pressure was brought upon the English, French and German Governments to prohibit its use. In France under Henry IV an edict condemned to death anyone found using this "pernicious drug" or "devil's food," as it was called.

Synthesis of Indigo

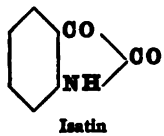
To Adolph Baeyer of Munich, the leading spirit and master of indigo research, the world owes more than any other the unraveling of the constitution of the molecule of indigo blue and the success in discovering methods to produce it synthetically on a commercial scale in competition with the natural product.

The vegetable product contains indigo blue, indigo red, indigo brown and indigo gelatin besides widely varying amounts of impurities. Of these indigo blue is the valuable constituent used in dyeing, and it almost is solely with this that the questions of constitution and production have been concerned.

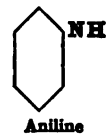
For nearly half a century Baeyer and his students have kept at work upon the problems connected with its economical production. The first successful product was offered on the market in the month of July, 1897, by the Badisch Aniline und Soda Fabrik. The commercial importance of the product three years later (1900), was such that the Director Brunck stated that in that year the firm had produced about 2,000,000 pounds of the synthetic indigo blue, an amount equal to that grown upon 250,000 acres of land in India.

As early as the year 1844 indigo had been the subject of research, and some progress had been made by the early investigators until 1865. The more profound work of Baeyer begins with this latter date. In the quarter of a century before he

began, it had been discovered that oxidation of indigo converts it into isatin; that distillation of indigo with potassium hydroxide produced aniline; that fusion with the same alkali yielded anthranilic acid, and nitric acid produced nitrosalicylic and picric acids, whose constitional formulas appear below:

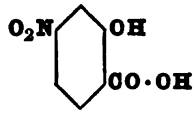


Isatin

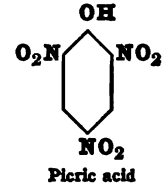


Aniline

Anthranilic (o-Aminobenzoic) acid

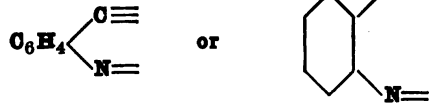


Nitrosalicylic acid



Picric acid

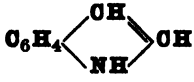
Now from the fact that these products resulted from the disintegration of the molecule of indigo, it could be gathered that indigo blue contained a benzene ring and further that attached to this ring there must be both carbon and nitrogen in the neighboring positions to each other, thus exhibiting the following nucleus as an actual constituent of the molecule of indigo blue.

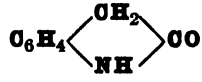


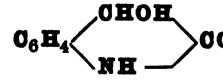
Nucleus known to exist in indigo blue previous to Baeyer's researches

As isatin was a product of the oxidation of indigo, it occurred to Baeyer that by the reverse process of reduction he might cause the molecule of indigo to form again. In the attempt to obtain it by this reduction he failed; but by the line of work then undertaken he discovered other substances such such as indol, oxindol, and dioxindol, and these were of great

service in helping to arrive at the constitution of indigo itself.

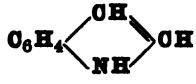

Indol

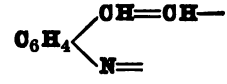

Oxindol


Dioxindol

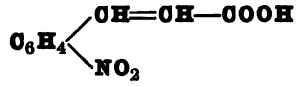
Baeyer believed that indol was a very close relative of indigo, and this was afterward proved to be true by Mencki, who in 1875 did obtain a very small amount of indigo blue by allowing ozone to act upon indol.

However, at this time, the clue suggested to Baeyer by the constitution of indol was that whatever substance was taken for the synthesis of indol must contain the same nucleus as indol itself, i.e.


Indol


Indol nucleus

A substance containing this nucleus was found by Baeyer and Emmerling in *o*-nitrocinnamic acid and in 1869 they succeeded in producing indol from this acid by fusing it with potassium hydroxide and iron filings. The function of the alkali was to eliminate a carbon atom and the iron was to do the same for the oxygen.

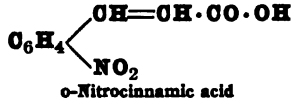

o-Nitrocinnamic acid

Firmly convinced of the close relation of indol to indigo blue, Baeyer hoped by starting with the same substance, *o*-nitrocinnamic acid, from which he had made indol to now form indigo blue itself by some modification of the process.

The modification was that he would attain the molecule of indigo blue through isatin instead of indol as the intermediate step; for although at first, as stated above, he failed to get indigo blue from isatin by simple reduction, he did

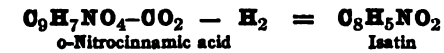
later succeed with the aid of acetyl chloride, phosphorus trichloride and phosphorus.

Comparison of the formulas of *o*-nitrocinnamic acid, indigo blue and isatin reveals the close relation of the three.



o-Nitrocinnamic acid

o-Nitrocinnamic acid — Indigo blue

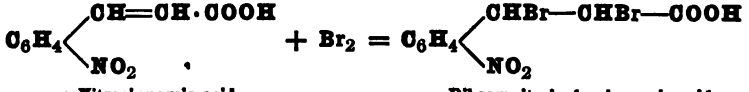


o-Nitrocinnamic acid — Isatin

Baeyer knew that *o*-nitrocinnamic acid could easily be made to give up carbon dioxide. Apparently the removal of two atoms of hydrogen and an atom of oxygen and the subsequent elimination of the easily removed carbon dioxide would result in the formation of indigo blue as indicated in the reactions above.

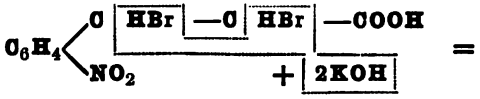
The attempt to eliminate these two hydrogens was successful, but since they could not be removed together with the oxygen as water, an indirect method was employed as follows:

The *o*-nitrocinnamic acid was first changed into bibromnitrohydrocinnamic acid by the action of bromine.

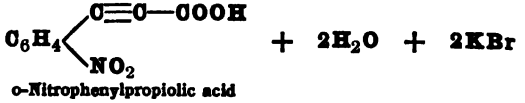


o-Nitrocinnamic acid — Bibromnitrohydrocinnamic acid

Now the two hydrogens were eliminated in combination as hydrobromic acid by treatment of this bromine product with alcoholic potash; the result is a new acid with two less hydrogens—*o*-nitrophenylpropiolic acid.



Bibromnitrohydrocinnamic acid



o-Nitrophenylpropiolic acid

This indirect elimination of two atoms of hydrogen from *o*-nitrocinnamic acid was most important in the synthesis of indigo blue. In comparison with isatin, this new acid merely contains one more molecule of carbon dioxide; in comparison with indigo blue it contains one more carbon dioxide and one oxygen atom, as shown in the following empirical formulas:

$$\underset{\text{o-Nitrophenylpropiolic acid}}{C_9H_5NO_4 - CO_2} \rightarrow \underset{\text{Isatin}}{C_8H_5NO_2}$$

$$\underset{\text{Indigo}}{C_9H_5NO_4 - CO_2 - O \rightarrow C_8H_5NO}$$

It now becomes apparent that to form isatin from this acid carbon dioxide must be removed and to form indigo oxygen in addition must be eliminated. By boiling *o*-nitrophenylpropiolic acid with potassium hydroxide Baeyer obtained isatin, and by another trial employing at the same time with the alkali a little grape sugar, as a reducing agent for the oxygen, he produced indigo blue itself.

This synthesis of indigo blue by Baeyer in 1880 after fifteen years of research is one of the most admirable triumphs of synthetic chemistry. The practical consequences were believed to be the ulitmate replacement of the natural indigo by the synthetic product and the highest hopes for its future were entertained. These hopes failed, however, of realization for a long time on account of the cost of the necessary materials and the poor yields of the technical processes.

When cinnamic acid is converted into nitrocinnamic acid, only a small per cent of the required ortho compound is formed; the paranitrocinnamic acid is useless for indigo manufacture. Even if the cinnamic acid is converted into the ester before nitrating and though this gives a yield of 70 per cent of the ortho compound still this is too small a yield for profit. Further when *o*-nitrophenyl propiolic acid is finally transformed into indigo blue, a part passes over into isatin instead.

The synthetic indigo blue prepared by this process did, however, work its way to some extent into commerce on account of the advantages it possessed for the calico printer of being

developed upon the cloth. It is only necessary to print the *o*-nitrophenylpropiolic acid upon the cloth and carry out the last steps of the Baeyer synthesis to convert the acid into indigo blue. For this purpose the best success has been obtained with sodium xanthogenate as a reducing agent and borax as the alkali.

In practice a paste consisting of *o*-nitropropiolic acid mixed with borax and sodium xanthogenate with starch for thickening is printed upon the cloth. Hanging the fabric up in a warm chamber then accomplishes the removal of carbon dioxide and the reduction of hydrogen simultaneously, when the indigo blue appears.

Constitution of Indigo

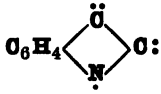
In the above synthesis, the empirical formula of indigo blue has been considered as C_8H_5NO, but in reality it is more complex than this, as was shown by E. V. Sommaruga. He determined the vapor density of indigo blue and from the result found that the formula must be double that of the empirical one employed previous to this date; consequently $(C_8H_5NO)_2$ is the correct formula.

The constitutional formula of indigo blue has passed through various phases of growth and correction according to new facts brought forth from time to time, until to-day there is a practical agreement in accepting the formula given below as the true one.

The evidence which has led to this structure of indigo blue may be summed up as follows:

1. The presence of a benzene ring in the molecule as shown by its easy oxidation into isatin, which contains such a ring.

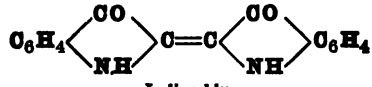
2. The easy formation of indigo blue from indoxyl and isatin is evidence of the presence of the following group, containing the benzene ring plus a second ring formed by the aid of a nitrogen and two carbon atoms:



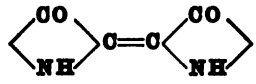
3. The vapor density corresponds to the molecular formula $C_{16}H_{10}N_2O_2$; therefore requiring two of the above groups in the true formula.

4. These groups must be joined together by a union of the carbon atoms numbered (1) so as to contain the larger group $C_6H_4—C—C—C—C—C_6H_4$, because *o*-dinitrodiphenyldiacetyl, which contains this nucleus, has been converted into indigo blue.

5. The nitrogen atoms are present as imide groups, as shown by the formation of N-diethylindigo from N-ethylpseudoisatin.



Indigo blue



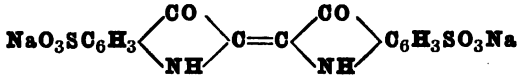
Chromophor

Indigo Blue as a Dye

Indigo blue is a solid substance of a deep blue color which appears in commerce from India in lumps, often bearing the impress of the cloths which have held it during the removal of water. These lumps are powdery, and crock the fingers in handling. When rubbed with some smooth, hard object, the lumps become burnished to a shining, coppery lustre which during the time of the alchemists caused it to be considered as a mineral or metal.

Indigo Blue on Wool. Indigo blue will not dissolve in water, and it possesses no salt-forming groups; it is in no sense a dyestuff. Salt-forming groups are introduced, however, by treatment with either hot strong sulphuric or cold fuming sulphuric acid, whereby sulpho acid groups

become lodged in the molecule and indigomonosulpho and indigodisulpho acids are formed. The latter of these, in the form of its sodium salt, is the indigo carmine of commerce. It is soluble in water and is suitable for dyeing wool mordanted with alum in a bath containing sulphuric acid. This treatment produced a shade upon wool long known as Saxony blue, though now nearly obsolete.



Indigo carmine

A more lasting and brighter shade of blue is produced by subjecting wool to the process described below for cotton with caution against a harmful amount of alkali.

Indigo Blue on Cotton. Cotton has no affinity for the soluble form of indigo employed upon wool. Though it is stained blue by immersion in a bath of indigo carmine, the color is easily washed entirely away with water.

To dye cotton, indigo blue must be converted into its leuco compound, which dissolves in an alkaline solution. In this soluble form and dissolved in an alkaline bath the colorless indigo white easily penetrates the cotton fibre, and on removing it from the vat the oxygen of the air at once oxidizes it to indigo blue.

The preparation of the vat for dyeing cotton requires the finest pulverization of the indigo blue and a production of nascent hydrogen in contact with the fine dyestuff in the vat. Less than one per cent of hydrogen (.84 per cent) suffices to change completely the nature of the insoluble indigo. It loses its color and changes to white by the fixation of two atoms of hydrogen; it becomes soluble in an alkaline liquid, and from being neither acid nor base in character, it becomes acid in nature and forms salts which will dissolve in water.

The requisite hydrogen may be furnished in a variety of ways with the necessary condition of maintaining the bath alkaline. An old method, widely used for a long time, employed the decomposition of organic matter by fermenta-

tion to evolve the hydrogen. Molasses and bran were placed with the finely divided indigo in the vat of water.

So vigorous a fermentation was caused that the evolved gas caused a blue froth to appear over the surface of the liquid.

Another method of obtaining hydrogen cheaply employed ferrous sulphate (copperas) and milk of lime. The ferrous hydroxide thus formed became oxidized to the ferric hydroxide at the expense of the water and released hydrogen.

$$FeSO_4 + CaO_2H_2 = CaSO_4 + FeO_2H_2$$

$$FeO_2H_2 + H_2O = FeO_3H_3 + H$$

Zinc dust and sodium hydroxide also produce nascent hydrogen in an alkaline solution. Sodium zincate remains dissolved in the solution.

$$Zn + 2NaOH = \underset{\text{Sodium zincate}}{ZnO_2Na_2} + 2H$$

But of all methods that most widely employed to-day uses sodium hydrosulphite as the reducing agent.

The old vats for dyeing indigo blue upon cotton had to be of extra depth and partly under the floor of the dye-house to accommodate the sediment which must settle before the dye bath became clear enough for the immersion of the cotton. As the blue froth is brushed away, the liquid below will appear of an opaque greenish yellow when the reduction is proceeding satisfactorily. If the liquid appears a bluish yellow, the reducing action has not proceeded long enough, and if the shade is reddish yellow too much alkali is present.

The process of dyeing cotton yarn consists in passing the moistened "chain" in at one end of the prepared and settled vat so as to go under a roll near the bottom but above the sediment, then to a roll at the other end of the vat but at the same level and back and forth from end to end by aid of other rolls at higher levels until the fibre is uniformly saturated with the indigo white solution.

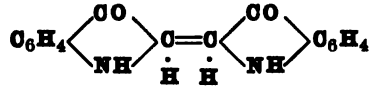
It then emerges from the end of the vat opposite to the one where it entered. The color of the yarn is greenish yellow

as it starts on a long trip over various rolls high up in the air, and the color rapidly deepens to a blue as the oxygen converts the soluble indigo white into the insoluble indigo blue in the fibre. If a deeper shade is desired it is only necessary to repeat the operation of passing it again through the vat and airing it until the proper depth of blue is secured. To neutralize the alkali retained by the yarn, it is passed through a bath containing weak acid and then into another of water to thoroughly cleanse it.

However the hydrogen may be produced in the vat, its action is always the same and the change in the indigo blue is represented as follows:

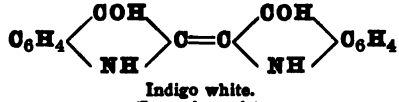
$$\underset{\text{Indigo blue}}{C_{14}H_{10}N_2O_2} + 2H = \underset{\text{Indigo white}}{C_{14}H_{12}N_2O_2}$$

These hydrogen atoms were formerly supposed to attach themselves to the two central carbon atoms of the molecule thus:



Indigo white.
(Old formula)

But because it has been discovered that indigo white possesses the properties of a phenol, which necessitates the union of this hydrogen with oxygen to form a hydroxyl group, the position of the added hydrogens has been changed, as shown in the later formula:



Indigo white.
(Later formula)

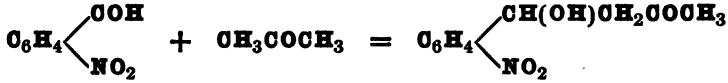
This indigo white exhibits acid properties by virtue of its hydroxyl hydrogen and it can form salts in alkaline solution. These hydroxyl hydrogens are in such unstable condition that they are instantly removed on exposure to the oxygen of the air.

Indigo white may be obtained as a white crystalline powder by the addition of hydrochloric acid free from all traces of air to its alkaline solution. It may be separated from the liquid by filtration and drying; both operations, however, conducted in an atmosphere of pure carbon dioxide or some other inert gas. Indigo white dissolves in alcohol, ether, and in solutions of the alkalies, forming yellow-colored liquids. The alcoholic solution shows a blue fluorescence.

Synthetical Production of Indigo from *o*-Nitrobenzaldehyde

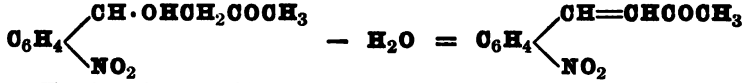
The known tendency of aldehyde and ketones to condense with one another was made use of by Baeyer and Drewson to produce a substance that could be easily transformed into indigo blue.

They brought together *o*-nitrobenzaldehyde and acetone which condenses to form *o*-nitrophenyl-lactomethyl ketone as follows:



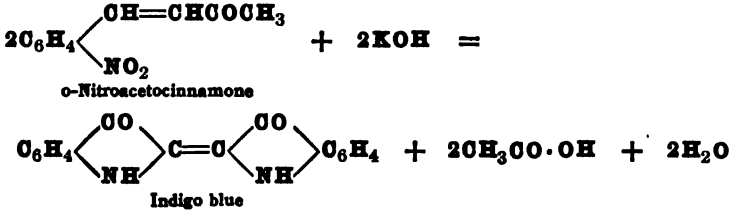
o-Nitrobenzaldehyde acetone — o-Nitrophenyl-lactomethyl ketone

By eliminating the elements of water from the hydroxyl and the neighboring methylene group *o*-nitroacetocinnamone is formed:



o-Nitrophenyl-lactomethyl ketone — o-Nitroacetocinnamone

This latter compound in the presence of alkalies and atmospheric oxygen changes at once into indigo blue.



o-Nitroacetocinnamone

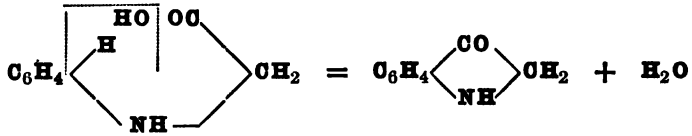
Indigo blue

This method has been used for producing indigo blue on the fibre in calico printing. The firm of Kalle & Co. have placed a colorless crystalline compound upon the market under the name of indigo salt T, which is a sodium bisulphite compound of the *o*-nitrophenyl-lactomethyl ketone. After printing this upon the fabric, the blue color is developed by passing it into a strong alkaline bath and then exposing to the air. Water and acetic acid are thus eliminated and indigo blue developed.

This method labors under the commercial disadvantage of a lack of sufficient toluene, which is the starting point for the manufacture of the *o*-nitrophenyl-lactomethyl ketone needed in this synthesis. There is not sufficient toluene available to replace by this process the natural indigo consumed by the technical world. Other synthetical methods of conversion of toluene into *o*-nitrobenzaldehyde have been discovered, but this leads to no increase of the insufficient raw material.

Heumann's Synthesis of Indigo Blue

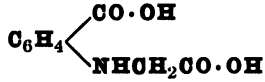
Professor Heumann of Zurich employed a method involving a radical departure from previous methods of attacking the problem of making indigo blue synthetically. The earlier workers employed bisubstitution products of the ortho-benzene series of compounds. Heumanne mployed a mono-substitution product and he discovered in phenylglycocoll a substance which reacts with fused potassium hydroxide to form a bisubstitution product of benzene. This new product is ketoindoxyl:



Phenylglycocoll Ketoindoxyl

It will be seen at once that we have here a half indigo molecule plus two hydrogen atoms. This hydrogen is so easily removed that on exposure to the air it is removed by the oxygen to form water and the residues unite to form indigo blue.

On account of the low yield of indigo blue by this method, it is hardly of more than theoretical interest, but a greater importance attaches to a derivative of this phenyl glycocoll, called *o*-phenylglycocoll carboxylic acid.

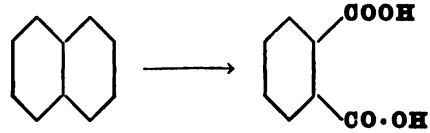


o-Phenylglycocoll carboxylic acid

The Badische Aniline und Soda Fabrik have for a score of years worked persistently upon the problem of producing a synthetic indigo blue which should compete successfully from a commercial standpoint. They now employ the Heumann synthesis, but modified so as to start with the cheaper substance naphthalene.

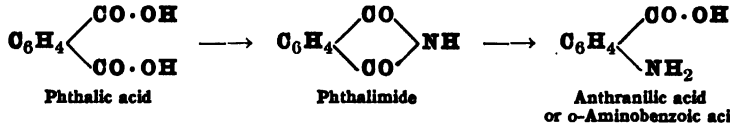
Naphthalene is oxidized to phthalic acid by strong sulphuric acid together with metallic mercury. The discovery of the importance of mercury was purely accidental. The yield of phthalic acid by using sulphuric acid alone was very unsatisfactory and every effort was made to ascertain the most favorable conditions for increasing the yield. One day on return from lunch the chemist engaged upon this research found the operation conducted during his absence a very much larger yield than usual and he sought in vain for the cause of this most astonishing and gratifying result. Persistent questioning of the assistant at last revealed the fact that during the heating of that particular quantity the assistant had broken a thermometer as he was stirring the hot mixture of naphthalene and acid and the mercury had gone into the liquid.

This was most fortunate, and the process now never omits the mercury, which so increases the yield that this is now one of the cheapest processes of the art.

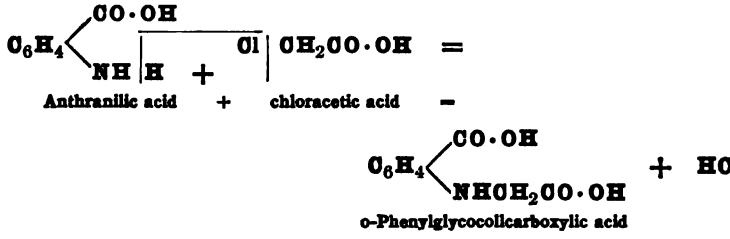


Naphthalene Phthalic acid

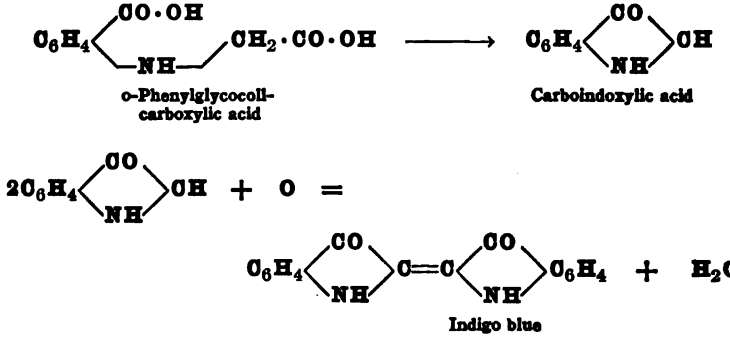
This phthalic acid is next converted into phthalinide first by the influence of heat and then by ammonia: sodium hydroxide and chlorine then transform this product into anthranilic or *o*-aminobenzoic acid, as shown in the scheme below:



When the chloracetic acid reacts with anthranilic acid *o*-phenylglycocollcarboxylic acid is formed and this leads at once upon the track of the Heumann synthesis.



It is but a step from this last substance to indigo blue itself and this conversion is effected by heating it with sodium hydroxide; an intermediate phase of the reaction is carboindoxylic acid; the alkaline solution precipitates indigo blue on treating it with a current of air.



It is to be regretted that Heumann did not live to see his method brought to a commercial success. The advantages of this process lie in the amount of naphthalene which is sufficient to replace all the natural indigo and in its cheapness, though its price has doubled within a comparatively short time.

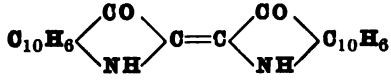
Indophor. Under this name there has been sold for a long time a grayish green powder. This is the carboindoxylic acid mentioned above. It is used for producing indigo blue in calico printing.

Among other syntheses one by R. Blank starts with chlormalonic ester which is condensed with aniline to furnish the benzene ring. The anilide thus formed is converted into carboindoxylic ester and this by saponification and oxidation is readily changed into indigo.

Sandmeyer originated a synthesis which starts with chloral $CCl_3.CHO$ and employs hydroxylamine and introduces the benzene ring in the form of aniline.

Naphthalene Indigo

It is of interest to note that employing the Heumann synthesis upon the naphthalene glycocolls produces varieties of indigo containing two naphthalene radicals in place of the usual benzene rings. By this change in composition



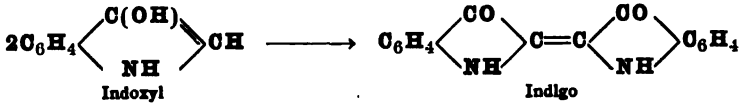
Naphthalene indigo

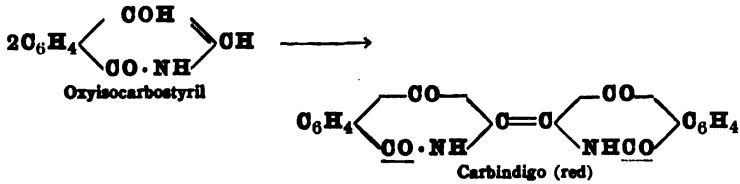
the color is changed from blue to green. These can be produced with a good yield, but have little technical value.

Indigo Red

Recalling to mind that indoxyl may be oxidized to indigo blue, it will be seen that a carbonyl derivative of indoxyl called oxyisocarbostyril could undergo a like oxidation and condensation to a substance analogous to indigo blue but

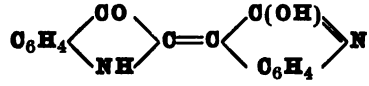
containing two carbonyl groups. Gabriel and Colman prepared such a derivative of indigo and gave the name of carbindigo, a red compound.





Carbindigo reacts like indigo when subjected to reduction and oxidation.

Indirubin, indigopurpurin is an isomer of indigo blue and may be prepred by mixing weakly alkaline solutions of indoxyl and isatin. Baeyer and Emmerling, who prepared this, called it an indogenide of isatin.



Indirubin or indigopurpurin

It is possible that this synthetic product is identical with the indigo red found in the natural indigo.

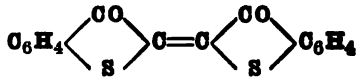
The Indigo Reds, or the Thio-Indigo Dyes

The splendid qualities of indigo have been esteemed for so many centuries that a new dye of any other color which could claim close relationship with it would fall heir to a large share of the enduring appreciation of that celebrated dye.

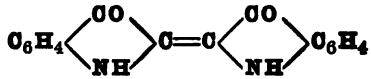
Two red dyes have lately appeared upon the maket from the firm of Kalle & Co. which are closely related to indigo. These dyes are known as thio-indigo red B and thio-indigo scarlet R. They contain sulphur (*θείον*, Greek for sulphur) as the name would indicate.

Upon the market, these dyes appear in the form of red pastes which contain 20 per cent of insoluble coloring matter. They are reduced by agents furnishing nascent hydrogen to leuco compounds that will dissolve in alkaline liquids. Hence they are applied in a manner similar to indigo by the vat method.

Thio-indigo red B has the following formula, wherein it will be observed that two imino groups (=NH) have been replaced by two sulphur atoms with a resulting change of color from blue to red:



Thio-indigo red B.



Indigo blue

Thio-indigo red B is also soluble in sodium sulphide and at the same time undergoes reduction so that it may be employed for dyeing in a manner similar to that for the sulphur dyes. This method, however, produces a shade inferior in quality to that produced from the vat process.

CHAPTER XVII

THE SULPHUR DYES

THIS class of dyes is at once one of the most valuable and the least understood. Their extensive development and application are comparatively recent; they are insoluble in water, are not capable of being refined by any known method of crystallization and are rapidly oxidized in moist condition by the air; hence the little present knowledge of their chemical constitution.

They derive their name from the fact that sulphur either alone or with caustic alkali or alkali sulphide is used in the preparation of almost all of them.

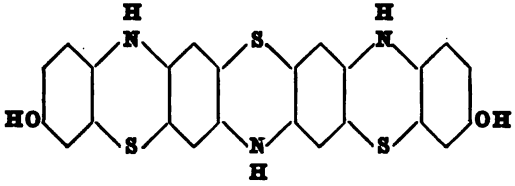
These dyes dissolve, however, in solutions of sodium sulphide. From these solutions unmordanted cotton extracts the dye which on subsequent exposure to the air is oxidized to an insoluble fast color in the fibre; the process is exactly analogous to that of indigo dyeing. In the solution of sodium sulphide, it is supposed that the dye is present as a leuco compound which the oxygen of the air converts into the dye.

A single dye of this class was discovered in 1873 and for some unaccountable reason no further work was done upon the sulphur dyes for twenty years. This first dye, called by its discoverers Croissant and Brettonière, ("Cachou de Laval") resulted from their having fused sawdust, bran, and even animal and human excrement with sodium sulphide. In spite of its offensive odor, it found extensive employment in dyeing unmordanted cotton a greenish yellow, which turned brown by atmospheric oxidation. Susbequent treatment with metallic salts made this shade exceedingly fast to acids, alkalies, washing and fairly resistant to light, but not to the action of chlorine.

The sulphur dyes which are once oxidized by the air are insoluble and lose their power of dissolving again in sodium sulphide solutions. Indeed the character of the dye is wholly changed.

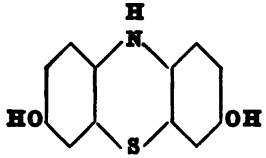
Vidal's Black. In 1893 Vidal made an important advance in the manufacture of sulphur dyes when he fused the polyatomic phenols and quinones with sodium sulphide. Later he employed *p*-phenylenediamine and *p*-aminophenol. The last-named substance yielded the valuable Vidal black when it was fused with sodium polysulphide, or its equivalent, sulphur and sodium sulphide. This has found extensive employment.

Vidal believed his black dye to have the following constitution:



Vidal black (?)

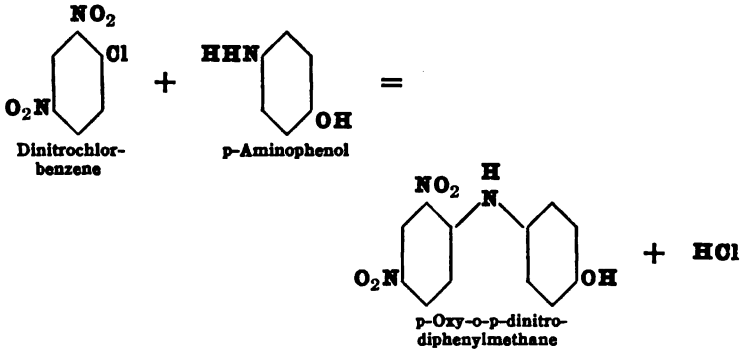
and his belief was based upon the fact that Bernthsen's dioxythiodiphenylamine was found to be an intermediate product if only a lower temperature was employed for the fusion. Its formula is:



Dioxythiodiphenylamine

Immedial Black V. (1897). Further advance was made by firm of Casella & Co. in Frankfort, which introduced of many the sulphur dyes under the name of "immedial dyes." Their immedial black V resulted from the fusion of *p*-oxy-*o*-*p*-nitrodiphenylamine with sodium sulphide and sulphur. This substance was prepared by the action of dichlornitrobenzene

upon *p*-aminophenol, which may be carried out with the aid of sodium acetate in either water or alcohol. The reaction is as follows:

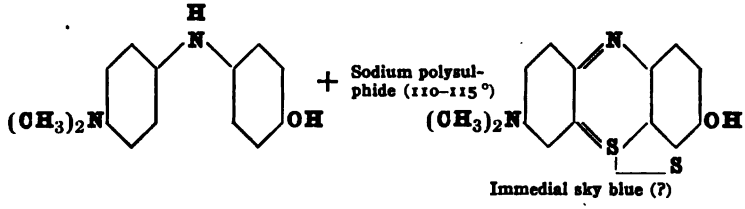


The fusion of this product with sulphur and sodium sulphide yields the immedial black V.

Immedial Blue. Oxidation of immedial black V before it has become fixed upon the fibre by hydrogen peroxide or steam and air converts it into immedial blue, another valuable shade.

Vidal Black S. is the Vidal black which has been treated with sodium bisulphite.

Immedial Sky Blue is a sulphur dye which results from fusing dimethyl-*p*-amino-*p*-oxy-diphenylamine with sodium polysulphide at 110° to 115°.



The most important sulphur dyes are the blacks and browns, though there are also found among them blue, green, yellow and orange dyes; red is lacking. The substances used for various examples of these dyes are given below:

St. Denis Black (1894) results from the fusion of *p*-phenylenediamine with sodium polysulphide. It dissolves in water containing alkali or alkali sulphide with a bottle-green color from which hydrochloric acid throws down a brown precipitate. Caustic soda turns the solution bluer.

Unmordanted cotton is dyed shades from grayish blue to black.

Sulphine Brown (1898) is an example of sulphur acting upon organic substances containing no nitrogen. To make it, oils, fats, or fatty acids are melted with sodium polysulphide. It dissolves in water to a dark-green solution. Hydrochloric acid causes a complete precipitation, meanwhile disengaging hydrogen sulphide. Caustic soda makes no change.

Unmordanted cotton is dyed a dark brown, which is changed by oxidizing agents to a reddish brown. The various shades resist the action of soap, acids and light, but not that of chlorine.

Italian Green (1895). The mixture of substances melted together for this dye consists of *p*-nitrophenol, caustic soda, sulphur and copper sulphate. The dye is a black mass resembling coke. The green solution in water oxidizes by exposure to the air, letting fall a green precipitate. A black precipitate and the evolution of hydrogen sulphide results upon adding hydrochloric acid.

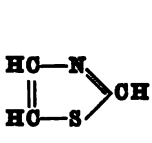
Unmordanted cotton is dyed a dull green which is very fast to light; it also resists washing and alkalies but not acids.

Printing Black for Wool (1896) is produced by mixing 1:8-dinitronaphthalene and 1:5-dinitronaphthalene and suspending in an alkaline solution of glucose containing sodium sulphite. Reduction takes place and the dye is formed as a bluish-black powder. Water dissolves it easily with a violet color which is changed to a bluish green solution by caustic soda.

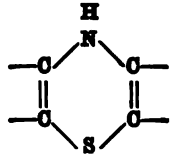
Wool is dyed a violet black from an acid bath; the dye is also used in wool printing.

Other sulphur dyes upon the market are cotton black D, thio cotton black, thiocatechine P, thiocatechine S, cotton brown, autogene black, auromal black, thional black, cross dye black, fast black B, fast black B.S, kryogene blue, printing blue for wool, anthraquinone black, etc.

Remarks upon the Sulphur Dyes. It is now believed, that the sulphur dyes contain one or more groups of organic disulphides which are converted by Na_2S into soluble mercaptans. These mercaptans have a direct affinity for the cotton fibre and are oxidized during the dyeing operation to the original disulphide. Sulphur dyes appear to contain certain chromophore groups (thiazole and thiazine):



Thiazole



Thiazine group

The thiazole grouping is found especially in the yellows and the thiazine in the immediate black. The Badische Company has discovered a new series of thiosulphonic acids obtained by the action of $Na_2S_2O_3$ on quinone. This series yields new blue sulphur dyes when fused with dimethyl-*p*-phenylenediamine $(CH_3)_2NC_6H_4NH_2$ sodium sulphide and sulphur. It seems probable that these dyes contain the thiazine grouping.

The Höchst Color Company has finally obtained red sulphur dyes containing the azine group by treating hydroxylated azines with Na_2S and copper salts.

Detection of Sulphur Dyes on Cotton. The presence of sulphur dyes on cotton is shown by boiling the sample with a ten per cent solution of caustic soda and, after rinsing, boiling it in a solution of stannous chloride. Hydrogen sulphide will be liberated if a sulphur dye is present.*

The primary materials for the manufacture of the sulphur dyes have been classified by Friedländer as follows:

Class I. includes the primary materials for the manufacture of the blues, violets, and blacks. These substances fall into three groups.

Group 1. Nitro and aminophenols.

* A. Wahl, Mon. Sci., Sept., 1907, 608–15.

Group 2. Nitro and hydroxy derivatives of diphenylamine.

Group 3. Indophenols or leucoindophenols; indamines or leucoindamines.

CLASS II includes the primary materials for yellows, browns. This class is made up of the *m*-diamines and their ring substitution-products containing a CH_3 group in the ortho-position; also the amines having in the meta-position some one of the groups NO_2, OH, SO_3H.

CHAPTER XVIII

MORDANTS

THE animal fibres silk and wool when dipped, without previous treatment, into solutions of coloring matter frequently absorb the color and hold it so firmly that it is retained during subsequent washing. Cotton on the contrary has far less power either to absorb the color, or to hold it so as to resist washing afterward. Many substances have the power to so affect the character of the cotton fibre that it then behaves more like silk and wool; it then absorbs the color and does not give it up again to water.

The substances which facilitate the dying of cotton in this way are called mordants (French *modre*, to bite), from the idea that they were capable of biting into or opening the cotton fibre so that the coloring material could enter and find so secure a lodgment within the fibre that it could not be removed by water.

Common alum is a mordant, and an illustration of its behavior toward a dye called carmine from cochineal will exhibit its precise function in making cotton retain the dye imparted to it. If alum is dissolved in water, the solution will remain colorless and transparent; addition of aqua ammonia will produce a white flocculent gelatinous cloud of aluminum hydroxide, according to the following reaction:

$$K_2Al_2(SO_4)_4 + 6NH_4OH = 2AlO_3H_3 + K_2SO_4 + 3(NH_4)_2SO_4$$

This hydroxide is white and makes the solution turbid until it finally settles to the bottom as a precipitate, leaving the liquid clear above it. If a little red cochineal extract be poured

into the same vessel containing the aluminum hydroxide, the contents well shaken and the precipitate allowed to settle again, it will be noticed that the aluminum hydroxide has seized the color and become stained by it, and on settling to the bottom the water is left colorless as before, all the red dye being extracted from the solution. This white gelatinous insoluble substance has a capacity which cotton has not, of fixing or uniting with coloring matter so as to hold it fast.

If an imperceptibly small amount of this gelatinous aluminum hydroxide could be first fixed in or on the cotton fibre, it could not be washed out, for it does not dissolve in water and the fabric thus enriched by this slight addition would assert the properties of aluminum hydroxide itself and absorb colors and hold them firmly.

This is just what is done in preparing cotton by the use of mordants. The cotton in the form of loose flocks or in the form of yarn or cloth is thoroughly and evenly saturated with a solution of alum, squeezed nearly dry and then passed into an alkaline solution of, e.g., sodium carbonate of the proper strength. At every point the particles of alum in the fibre are reached by the dissolved particles of the sodium carbonate and transformed into the white insoluble jelly-like aluminum hydroxide (or according to conditions a basic aluminum sulphate) as shown in the following equations:

$$K_2Al_2(SO_4)_4 + 3Na_2CO_3 + 3H_2O =$$
$$2AlO_3H_3 + K_2SO_4 + 3Na_2SO_4 + 3CO_2$$

The cotton is then washed without losing what it has gained by this treatment and the now mordanted fibre will absorb the various shades of color and hold them securely, beyond the power of water to remove.

There are many substances which are used as mordants, some white in themselves, others colored; of course the colored ones will modify the shade of the dye subsequently applied, and even the colorless ones often change the color of the pure dye. An example is furnished by aluminum hydroxide which, colorless itself, produces various shades of blue when dipped

into a solution of logwood; another colorless mordant, hydroxide of tin, precipitated on cotton develops shades of red when dipped into a similar solution of logwood. From this example it is evident at once that a single dyestuff may furnish the dyer with a variety of different colors according to the particular mordant employed.

The primary reason, however, for the use of a mordant is the imparting to ordinarily indifferent fibres the capacity of seizing and holding firmly the dyes that could not otherwise be retained.

Though silk and wool have been mentioned as fibres which easily become colored without the assistance of mordants, still these substances are sometimes needed, when their action is similar to that exhibited in the case of cotton. In alum, $K_2Al_2(SO_4)_424H_2O$, we have an example of a common mordant. The aluminum in this substance is the efficient agent, for its hydroxide is insoluble, and forms the true mordant. Other substances contain the same element, and oftentimes it is applied to the cloth in such a form that the process of ageing (exposure in a moist condition to the air) will produce an insoluble compound of aluminum ready to combine with a dye. Sometimes the acetate of aluminum, $Al(C_2H_3O_2)_3$, is used; for this salt easily lends itself to the process of ageing. This ageing consists in the decomposition of the aluminum acetate by the water which is present upon the damp fabric or in the steam that is used to hasten the ageing process. The final stage is reached when the acetate is all changed to aluminum hydroxide, the reaction for which follows:

$$Al(C_2H_3O_2)_3 + 3H_2O = AlO_3H_3 + 3C_2H_4O_2$$

John Thom was the first to observe that there is an elective affinity of the bases for the various coloring matters, that is, that the bases have a stronger attraction for some coloring matters than for others. An example of this may be seen in alumina, which has a stronger attraction for the principle of madder than for that of logwood, and a greater affinity for the latter than for quercitron. When a piece of cloth

impregnated with alumina is immersed in a decoction of quercitron bark, it acquires a fast yellow hue; but, if it is afterward well washed and then kept for some time in a hot solution of loowood, the alumina parts with the color of the quercitron to combine with that of the logwood, and the cloth changes from yellow to purple. If now it be digested for a few hours with an infusion of madder (hot), the coloring principle of the logwood is turned out, and the alumina unites with that of the madder, the cloth is now found to be red instead of purple. The amount of the alumina upon the fibre does not seem to be sensibly altered by these substitutions.

Character of the Textile Fibres

Wool Fibre. The wool fibre is both acid and basic in character, dissociating the salts used as mordants and combining with both the acid and the base of the salt. The reaction is most complete at the boiling temperature, but for the best results, the salts must not be decomposed until they have had time to penetrate into the fibre. Decomposition is retarded by the use of sulphuric acid, hydrochloric or oxalic acid or by tartrates and oxalates in conjunction with the mordanting salt.

Silk Fibre. Silk absorbs acids from their dilute aqueous solutions and retains them tenaciously (Rawson). Silk behaves like wool toward metallic salts used for mordants. It decomposes the salt even in cold solutions. Silk acts like wool toward coloring matters in general but has less affinity for acid colors and a greater for basic colors.

Cotton Fibre. Cotton, while it is the cheapest of the textile fibres, is at the same time the most difficult one to dye. This difficulty arises from the well-nigh indifferent character of the fibre. It betrays neither the properties of an acid nor a base and therefore exhibits little tendency to form salts with coloring matters in analogy to the action of wool and silk. Yet in some cases it does exhibit an activity strongly marked as when immersed in a solution of tannic acid it seizes it with great avidity and absorbs large amounts from the solution.

Among the most important inorganic mordants are those which are salts corresponding to the sesquioxide bases of the general formula R_2O_3. The salts of alumimun, chromium, and iron are the most prominent examples. There are many different salts of these bases in actual use and which particular one is to be used depends upon the kind of fibre to be dyed and the kind of dye itself to be applied. In all cases, the object sought by the dyer is to precipitate from the soluble mordant salt an insoluble residuum in the structure of the fibre itself, which later shall combine with an otherwise elusive coloring matter, turning it into an insoluble compound that will not wash away.

This insoluble residuum entrapped in the fibre is chemically different from the salt itself and it consists either of the hydroxide of the base or a very basic salt of the same base. Various means are employed for the fixation of this hydroxide in the structure of the fibre, but it is interesting to note that the fibres themselves often exert a sufficiently strong decomposing action without the usual addition of some alkaline reagent.

When, for instance, cotton fibres are steeped in an aqueous solution of alum, $K_2Al_2(SO_4)_424H_2O$, and then after drying replaced in pure water, a precipitate of the hydrate of aluminum is left within the cell-walls and tube without the presence of alkali. This is probably due to the dialytic action of the outer membrane of the fibre which allows the dissociated crystalloidal part of the alum to diffuse into the water while the colloidal insoluble hydroxide cannot escape.

The various insoluble precipitates formed by the combination of the hydroxides with the soluble dyes are usually known as lakes. Other metallic salts share with alum the property of so dissociating as to leave insoluble hydroxides in the fibre.

When wool, which by nature is both acid and basic, is immersed in a solution of alum, the wool combines with the acid and basic portions of the dissociated alum and this action of the wool is so strong that if left to itself the aluminum hydroxide would attach itself too fast and too irregularly to

the fibre so as later to cause uneven dying. To prevent this rapid decomposing action of the wool a certain amount of sulphuric acid as retarding agent may be used.

Aluminum Salts

Aluminum is an element which by the variety of its compounds and the instability of many of them exhibits a peculiar adaptability to the needs of the dyer. It forms normal salts in which its full valence of three is saturated by the radicals of the common acids, and it also forms basic salts wherein hydroxyl groups have replaced one or more of the acid radicals. This facility of forming basic salts is of the greatest value in many ways, for the properties of wool and cotton differ so much in their active influence on a solution of alum that when such a solution is used to mordant wool, free sulphuric acid or a similarly acting agent must be put in the solution to prevent aluminum hydroxide from being too rapidly deposited in the fibre and therefore unevenly. In mordanting cotton, on the contrary, the alum would be acted upon too slowly by the inert cotton and thus a compound of aluminum more easily dissociated is used and the compound then employed is one of the many basic salts of aluminum. Aluminum sulphate, having released a portion of its acid and taken hydroxyl in its place, is so much more susceptible of decomposition in aqueous solution than the normal sulphate that the inactive cotton can cause a deposition of the required amount of hydroxide in its own fibre.

I have spoken of basic aluminum sulphate as if there were but one; as a matter of fact there are many basic sulphates with varying proportions of acid and basic groups. Some are soluble and some insoluble; the latter of course cannot be used as mordants. Not only are many basic sulphates known, but basic acetates, basic chlorides and others, all possessing some particular advantage for some particular kind of dyeing.

The commonest and the oldest compound of aluminum, known as alum, is a translucent white crystalline substance

consisting, for about half its weight, of water of crystallization. The facility with which it crystallizes makes it easy to purify and this has kept it long a favorite form of aluminum in the art, for a slight amount of iron as impurity in aluminum compounds works great injury to many dyes. A further advantage arises from the presence of potassium sulphate, which remains in the solution when alkali or the ageing process is used to precipitate the hydroxide in the fibre; the mere presence of the potassium sulphate causes a greater degree of dissociation of the salt and a more abundant fixation of the insoluble residuum in the fibre.

Aluminum sulphate, $Al_2(SO_4)_3 18H_2O$ is now nuch prized and much used on account of its cheapness and purity. There is danger of the presence of iron and of free acid; furthermore, it is of more irregular composition than alum, but manufacturers have overcome these objectionable features and produce a pure article.

The basic salts may be produced by the addition of sodium hydroxide, sodium carbonate and sodium bicarbonate, also by other soluble hydroxides and carbonates. According to researches of Liechti and Suida, aluminum sulphate is decomposed by sodium carbonate and sodium bicarbonate as follows:

$$Al_2(SO_4)_3 + Na_2CO_3 + H_2O = Al_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2$$

a more basic sulphate where the aluminum suffers a greater loss of acid is formed according to the following equations:

$$2Al_2(SO_4)_3 + 6NaHCO_3 = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 6CO_2$$

A still more basic sulphate results as follows:

$$Al_2(SO_4)_3 + 4NaHCO_3 = Al_2(SO_4)(OH)_4 + 2Na_2SO_4 + 4CO_2$$

These basic sulphates are soluble in water, and their solutions are made by adding the proper proportions of aluminum sulphate and sodium carbonate or bicarbonate.

The cotton to be mordanted is immersed in the solution of basic aluminum sulphate; the cotton slowly decomposes the basic salt, precipitating aluminum hydroxide in the fibre; the more basic the sulphate used, the more hydroxide deposited. To hasten and also to increase the deposition the cotton may be passed through a weak solution of ammonia. This completes the removal of sulphuric acid from the basic salt by substituting hydroxyl groups in their place:

$$Al_2(SO_4)(OH)_4 + 2NH_4OH = 2AlO_3H_3 + (NH_4)_2SO_4$$

It is believed that aluminum sulphates exist still more basic in character than any of those given above, but they are insoluble, and it may be that these very basic and insoluble compounds fixed upon the fibre act as true mordants as well as the hydroxide of aluminum itself. By the increase of the basic character of these sulphates of aluminum, the integrity of the molecule is greatly disturbed. The normal sulphate cannot be decomposed either by boiling or by diluting with water; the basic salt, $Al_2(SO_4)_2(OH)_2$, dissociates slowly and incompletely; the more basic salt, $Al_4(SO_4)_3(OH)_6$, dissociates more easily and the still more basic salt, $Al_2(SO_4)(OH)_4$, breaks up very quickly on boiling or diluting with water, separating gelatinous aluminum hydroxide. In the presence of cotton, the instability of these salts is increased, much to the advantage of the mordanting processes.

Aluminum Acetates. The acetates, both normal and basic, distinguish themselves from the corresponding sulphates by their greater instability and consequent easier dissociation under the influences of heat and dilution on their aqueous solutions. The normal acetate has not been obtained in the free state as a solid. A solution of a salt of this formula $Al_2(C_2H_3O_3)_6$, may be made by dissolving aluminum hydroxide in acetic acid, but it is regarded as consisting of aluminum diacetate and acetic acid. Careful evaporation of this solution leaves a salt of this composition,

$$Al_2(C_2H_3O_2)_4(OH)_2$$

Solutions of the normal acetate are prepared by acting on aluminum sulphate with lead acetate; the lead sulphate falling as a precipatate is filtered off:

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + 3PbSO_4$$

According to Liechti and Suida, normal aluminum acetate is not dissociated by boiling or by dilution with water. By the addition of various proportionate amounts of sodium carbonate to solutions of the normal acetate, varying degrees of basicity may be obtained, as illustrated in the following equations:

$$2Al_2(C_2H_3O_2)_6 + Na_2CO_3 + H_2O = 2Al_2(C_2H_3O_2)_5OH + 2NaC_2H_3O_2 + CO_2$$

$$2Al_2(C_2H_3O_2)_6 + 2Na_2CO_3 + 2H_2O = 2Al_2(C_2H_3O_2)_4(OH)_2 + 4NaC_2H_3O_2 + 2CO_2$$

$$2Al_2(C_2H_3O_2)_6 + 3Na_2CO_3 + 3H_2O = 2Al_2(C_2H_3O_2)_3(OH)_3 + 6NaC_2H_3O_2 + 3CO_2$$

$$2Al_2(C_2H_3O_2)_6 + 4Na_2CO_3 + 4H_2O = 2Al_2(C_2H_3O_2)_2(OH)_4 + 8NaC_2H_3O_2 + 4CO_2$$

Doubling the formula in the second and fourth equations reveals the progressive action of sodium carbonate in forming the basic salt. The basic acetates thus obtained—more or less sodium acetate being present in each case—suffer dissociation on heating. The more basic the acetate, the lower the temperature of dissociation. If alkaline sulphates are absent, no dissociation is produced at the ordinary temperature by dilution with water. If alkaline sulphates are present, both the normal and basic acetates are dissociated by dilution with water, and more readily by heating. The precipitates formed by heating basic aluminum acetate in the absence of alkaline sulphates, do not redissolve on cooling; if alkaline sulphates are present, the precipitates thus formed do redissolve on cooling. When aluminum acetate is made

from alum in place of aluminum sulphate, the solution of course contains a soluble alkaline sulphate, potassium or ammonium sulphate:

$$K_2Al_2(SO_4)_4 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + K_2SO_4 + 3PbSO_4$$

The more common method of making basic aluminum acetate is by the combined action of lead acetate and sodium carbonate on a solution of aluminum sulphate:

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2PbSO_4 + Na_2SO_4 + CO_2$$

In both instances, a soluble sulphate is produced, and the aluminum acetate dissociates more easily. Where the slight amount of lead acetate remaining dissolved in the solution would be injurious, calcium acetate is used in place of lead acetate.

The ease with which aluminum acetates dissociate facilitates their use in printing upon cotton where a paste containing both the dye and mordant are simultaneously fixed upon the fibre, which later pass over heated rolls, or through a heated moist chamber. The heat and moisture cause the rapid disengagement of the volatile acetic acid with the production of aluminum hydroxide in the fibre which in turn seizes the dye and holds it fast in the tissue.

Cotton fabrics immersed in solutions of basic acetates need no alkalies to decompose the salt, for on passing the fabric through a warm moist room, acetic acid rapidly volatilizes, leaving the insoluble hydroxide, which is now ready to receive the dye.

Note. The acetate of aluminum, in decomposing by heat on the fibre, yields acetic acid, which helps to dissolve the alizarin and thus enables it to penetrate the fibres and combine with the aluminum hydroxide (Benedikt and Knecht, p. 207).

Aluminum Sulphate Acetates. These double compounds of aluminum with sulphuric and acetic acid radicals are

easily prepared and in many cases favorably influence the production of full and richer colors than either sulphates or acetates of aluminum alone. When less than the required proportion of lead acetate is used, then a double salt results, according to Liechti and Suida as follows:

The normal sulphate acetate does not dissociate on diluting its solution, but it does on heating, differing in this respect from both normal aluminum sulphate and normal aluminum acetate, neither of which dissociate on diluting or boiling.

The basic sulphate acetates dissociate both on diluting and on heating, the greater readiness to dissociate being shown by the more basic salts. The precipitates formed are gelatinous, and if the salt is not more basic than $Al_2SO_4(C_2H_3O_2)_3OH$, it redissolves on cooling. The aluminum sulphate acetates, normal or basic, yield nearly the whole of their alumina to the fibre during mordanting and ageing. In this respect they are much stronger mordants than the aluminum sulphates, and are of about the same strength as the basic acetates. The investigations of Koechlin, Schoach and D. Koechlin have shown that in mordanting with sulphate acetates, basic aluminum sulphate, and not aluminum hydroxide, is fixed upon the fibre.

Solutions of aluminum acetate and aluminum sulphate acetates, both normal and basic, are known as Red Liquor, because used in dyeing reds, and not from its own color.

Aluminates. In the above-mentioned compounds, the element aluminum is playing the part of a base-forming element; its hydroxide, AlO_3H_3, exhibits the function of a base by dissolving in acids to form salts of those acids, but in a different environment it can exhibit the functions of an acid-forming element, as when the gelatinous insoluble hydroxide dissolves in a solution of sodium hydroxide to form a salt known as sodium aluminate, as illustrated by the following equation,

$$AlO_3H_3 + 3NaOH = Na_3AlO_3 + 3H_2O$$

The acid character of aluminum hydroxide is weak and the aluminates in solution are easily decomposed by all acids,

even carbonic acid; aluminum hydroxide is precipitated, a salt of sodium or potassium remaining in solution. In a similar way, in solution, the aluminates are decomposed by ammonium salts, potassium or sodium salts, as the stronger bases combine with the acid of the ammonium salt, whereas the aluminum hydroxide does not combine with the ammonia, and it remains in the free state as a gelatinous precipitate:

$$Al(OH)_2OK + NH_4Cl = AlO_3H_3 + KCl + NH_3$$

Use is made of this reaction in fixing the mordant. Sodium aluminate occurs in commerce as a lumpy powder of a slightly greenish-white color. It is readily soluble in water, but not deliquescent and is decomposed by carbon dioxide in the moisture. It is used for a mordant on cotton piece goods, but cannot well be used on cotton yarn on account of its caustic action on the hands of the workmen. Sodium aluminate offers the great advantage that it does not carry iron into the ultimate color, and that it is fixed on the fibre in a short time without ageing. It finds but limited employment as it cannot be used with acid mordants. The goods are simply impregnated with the aluminate, rapidly dried at an elevated temperature, and passed through a solution of ammonium chloride at 50 to 60° C. The aluminum is thus fixed as aluminum hydroxide. Sodium aluminate is not used as a mordant for silk or wool because it is too alkaline for those fibres. For the production of lakes, the coloring matter is mixed with a solution of sodium aluminate and precipitated by the addition of sulphuric acid. These lakes are considered by Morin to be richer than those obtained from alum, and are produced at one-half the cost.

A number of other compounds of aluminum are prepared and used as mordants in special cases. Aluminum chlorides, normal or basic, yield little aluminum hydroxide to the fibre and they attack vegetable fibres so that they are not suitable for mordants. They are made use of as carbonizing agents for destroying vegetable fibres in wool. The mixed material is placed in a solution of the normal chloride, the excess of the

liquid removed and the material dried. The disintegrated vegetable fibres are removed as dust by shaking.

Aluminum Thiocyanate, $Al(CNS)_3$, can be boiled in solution without decomposition, and the salt, $Al(CNS)_2OH$, is also stable, but the more basic salts are decomposed on boiling; mere dilution will not cause the decomposition of any of these salts.

It possesses the great advantage that it does not attack the steel doctors of the printing machines, and thus does not introduce iron into the printing color; hence the purity and brilliancy of the alizarin is preserved. The high price of the article has prevented its more general employment. Aluminum thiocynate may be obtained by the double decomposition of aluminum sulphate and barium thiocyanate:

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = 2Al(CNS)_3 + 3BaSO_4$$

Aluminum Chloride Acetate, $Al(Cl)(C_2H_3O_2)_2$, yields according to Liechti and Suida only 3¼ per cent of its alumina to the fibre, after steaming, drying and ageing. It has been obtained from aluminum sulphate, lead acetate and barium chloride solutions. It does not dissociate on diluting or heating.

Aluminum Nitrate Acetate is produced by the double decomposition of aluminum sulphate with acetate and nitrate of calcium or lead.

Chromium Mordants

Chromium exhibits in its various compounds the double function of an acid and a base-forming element. The hydroxide of chromium is a greenish gelatinous insoluble substance which dissolves in acids to form salts,

$$2CrO_3H_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O$$

Here it shows its marked basic property, but when in the presence of sodium hydroxide it likewise dissolves, forming easily decomposable salts, called chromites, where chromium is a weak acid-forming element.

Potassium Bichromate, $K_2Cr_2O_7$. The most common and the most important compound of chromium is potassium bichromate; here the chromium acts as an acid-forming element. This salt suffers decomposition when wool is immersed in its solution, the extra chromium anhydride combining with some constituent of the wool, and allowing the normal potassium chromate to remain in the solution. This chromium anhydride CrO_3 is not in the proper form for a mordant, and in some way it must lose oxygen and become reduced to the lower oxide Cr_2O_3, which in the hydrated form is a true mordant. The wool itself exerts some reducing action on it, but usually this process is completed by some organic reducing agent like tartaric or oxalic acids simultaneously used, which by abstracting oxygen in the presence of water converts the CrO_3 to the hydrate CrO_3H_3

$2CrO_3 = Cr_2O_3 + 3O$ (used up in oxidizing the tartaric acid).

Thus the object of the process is to fix chromium hydroxide in the fibre, which so charged in turn fixes the dye.

Chromium Sulphate, $Cr_2(SO_4)_3$, similar in its behavior to aluminum sulphate, is used to furnish by its decomposition chromium hydroxide to the fibre. It may be made by dissolving chromium hydroxide in sulphuric acid. From this solution on evaporation violet blue cyrstals of the composition $Cr_2(SO_4)_3 15H_2O$ may be obtained. A solution of chromium sulphate is not decomposed by dilution or boiling or by both actions exerted simultaneously. Solutions of chromium sulphate give precipitates of chromium hydroxide when acted upon by sodium hydroxide; an excess of the latter redissolves the precipitate which, however, is thrown down again by boiling. By the addition of sodium hydroxide to solutions of chromium sulphate, in amount insufficient to produce the normal chromium hydroxide, basic sulphates may be formed analogous to the aluminum sulphates of varying degrees of basicity. They vary in stability according to their basicity and the presence of alkaline sulphates. Boiling does not decompose the basic sulphates, but dilution

does; the more basic the more easily they are decomposed. Chromium sulphate is not used as such but in combination as chrome alum. This salt $K_2Cr_2(SO_4)_424H_2O$, is produced when a mixture of potassium bichromate, sulphuric acid and some reducing agent, as alcohol, sulphurous acid, etc., is heated.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O = K_2Cr_2(SO_4)_424H_2O$$

A peculiarity of basic chromium sulphates in comparison with corresponding basic aluminum salts is their behavior with alkaline sulphates; these cause the aluminum salts to dissociate more readily, giving aluminum hydroxide to the fibre; the alkaline sulphates retard the dissociation of basic chromium sulphates. Consequently basic salts of chromium made from chrome alum do not dissociate so easily as those made from chromium sulphate, the presence of alkaline sulphate causing increased stability.

Chromium Thiocyanate, $Cr(CNS)_3$, has an especial advantage in printing on cotton for developing brilliant and fast blacks with logwood.

The normal salt does not dissociate on boiling or on diluting. By the addition of sodium hydroxide in proper porportions basic salts of considerable stability are formed. The normal salt yields only 5 per cent of chromium to the cotton fibre while a basic salt $Cr_2(CNS)_2(OH)_4$ yields about 34 per cent of its available chromium to the fibre. This salt is used by calico printers for the production of steam logwood blacks which are very brilliant and fast colors.

Basic Chromium Acetates. The salts $Cr_2(C_2H_3O_2)_5OH$ and $Cr_2(C_2H_3O_2)_2(OH)_4$ together with intermediate compounds have been prepared by treating lead acetate with basic chromium sulphate. These salts dissociate with difficulty, but with more ease on boiling and diluting the more basic they are.

Chromium Chloride Acetates. The compound $Cr_2(C_2H_3O_2)_4Cl_2$ and others are obtained by dissolving basic chromium chloride in acetic acid or by the action of calcium acetate and calcium chloride on chrome alum. The most basic salts only show a tendency to dissociate on heating and diluting. The

salt $Cr_2Cl(C_2H_3O_2)_2(OH)_3$ yields to the cotton fibre in mordanting 50 per cent of its chromium. (Liechti and Schwitzer.)

Other compounds of chromium are made and used for special purposes or because they have given fine effects in the hands of certain men who have given time to the study of their peculiar properties.

Iron Compounds

Ferrous acetate is one of the iron compounds that is of most assistance to the dyer. The normal salt $Fe(C_2H_3O_2)_24H_2O$ may be made by the action of a solution of lead acetate upon ferrous sulphate or by dissolving iron in acetic acid. The salt crystallizes in green monoclinic prisms which quickly oxidize on exposure to the air, to basic ferric acetates, hence its solution is too unstable to be used as a mordant.

Pyrolignite of iron, known as iron liquor or black liquor, is an impure ferrous acetate which in practice is found much more pure than the pure salt, and it is a valuable mordant. It is prepared by treating scrap iron with pyroligneous acid (crude acetic acid). The tarry matters which rise to the top of the vat are skimmed off. The liquid contains besides the essential ingredient ferrous acetate, some ferric acetate and tarry matter. The iron salt of pyrocatechin, which is present together with other empyreumatic substances is considered by Moyret to be the substance which prevents the oxidation of the liquid.

Pyrolignite of iron is used in *cotton* dyeing, in greater quantities in *calico* printing and in black *silk* dyeing.

Ferrous Sulphate. This substance forms green crystals known as green vitriol. The crystals effloresce, on exposure to the air, turning white and later as oxidation proceeds changing to brown basic ferric sulphate. Ferrous sulphate is one of the oldest mordants and is largely used in *wool* dyeing. It is used to a considerable extent in cotton dyeing, also for the production of Prussian blue in calico printing and for the formation of *chamois* yellowish brown color on cotton by the action of sodium carbonate.

Organic Mordant. Tannic Acid

Tannic acid is one of the most important mordants for *cotton*, and enormous quantities of it are used in preparing that fibre to receive coloring matter. Cotton, though to decompose the more basic metallic mordants of aluminum and chromium, is very indifferent to these in comparison with its strong affinity for tannic acid, which it seizes from aqueous solution and holds fast within the fibre.

It is a vegetable product found in many species of plants in the form of a glucoside (?) which upon extraction from the vegetable tissue containing it and boiling with dilute acids breaks up, forming tannic acid and sugar. It exists in gall-nuts, sumac and other tannin matters and it may further be prepared synthetically by the condensation of two molecules of gallic acid.

$$2C_6H_2\begin{Bmatrix} OH \\ OH \\ OH \\ CO\cdot OH \end{Bmatrix} = C_6H_2\begin{Bmatrix} CO\cdot OH & HO \\ OH & HO \\ OH & HO \\ O- & CO \end{Bmatrix}C_6H_2 + H_2O$$

It is most readily obtained from gall-nuts. It comes into the market in small buff-colored scales. The purest and best tannic acid is made from gall-nuts in the following manner: The crushed galls are heated with water to form a concentrated solution, the temperature ranging from 40 to 60° C. When the liquid is sufficiently concentrated, it is run off and allowed to settle twelve hours. It is then run through a filter into a closed drum in which it is agitated with one-quarter its volume of ether (.750 sp.gr.) for several hours. The emulsive liquid thus produced is run into closed tanks and allowed to remain at rest from eight to ten days, during which time it gradually separates into two parts. The upper ethereal layer, which contains the impurities, is drawn off, and the ether removed by distillation, the lower layer being also separately distilled to recover the ether until it acquires a syrupy consistency.

CHAPTER XIX

VAT DYES

Derivatives of Indigo and Anthracene

The reputation of indigo and alizarin of great antiquity before the discovery of the synthetic dyes derived from coal-tar made it a matter of great interest to discover whether derivatives of the dyes would produce other colors, and further whether these new colors might possess the same qualities which had made the old dyes so valuable.

When coal-tar products became so prolific in dyes of all colors, attempts were made to prepare indigo and alizarin from coal-tar sources independent alike of the indigo plant and of the madder root—the source of alizarin. These attempts often in vain were after years of study and ceaseless investigation so successful that to-day synthetic indigo and alizarin rival the purity of the natural products. Indeed no madder root for alizarin has been cultivated for many years, and the area in India devoted from time immemorial to the cultivation of the indigo plant shows a shrinkage of a quarter of a million acres.

It is needless to speculate upon the advantage of releasing great areas of arable land formerly demanded for the cultivation of the madder root in Europe and for the indigo plant in India while agriculture is in such straits to produce the food grains of the world.

The history and the methods for producing indigo and alizarin from coal-tar products are detailed in the preceding chapters. This chapter will be devoted to the synthetic derivatives of indigo and anthracene.

The vat dyes are valued for their fastness or permanence, not alone against the action of alkalies, acids and washing but also against the influence of light bleaching and other agents.

Since they are insoluble in water and because a fine state of division is requisite, they are usually sold as pastes containing upwards of 20 per cent of the actual dye.

Indigo is the oldest vat dye, and the principle of vat dyeing in general will be understood by describing how indigo is dyed upon cotton or other fabrics.

Indigo blue or indigotine is insoluble in water and so cannot be used as a dye in its natural condition. However, when indigo in a finely divided state or in the paste form is placed in an alkaline liquid in which nascent hydrogen is being evolved, the indigo gradually loses its blue color and its insoluble character; it dissolves in the alkaline liquid at the same time. The product so made is indigo white and it is present as a soluble sodium salt in the solution which is transparent but at the same time changed to a greenish-yellow color. If a few drops of this liquid are allowed to fall upon white paper, the oxygen of the air changes it almost instantly back to the original insoluble indigo blue.

Now loose cotton or cotton yarn immersed in the greenish-yellow alkaline solution is able to take up into its fibres the soluble indigo white and when lifted from the vat, the oxygen of air immediately works upon it changing the absorbed dye to a blue which is insoluble and securely held within the fibre.

To obtain a deeper shade the cotton may be immersed again, and again exposed to the air; this operation is repeated if necessary until the desired depth of blue is attained. The mechanical details of the dyeing process cannot be described here.

Indigo is a vat dye; alizarin, however, is not a vat but rather a mordant dye. Yet the new colored derivatives of alizarin and anthraquinone and anthracene are in many instances true vat dyes as well as the new colored derivatives of indigo.

Indigoid Dyes

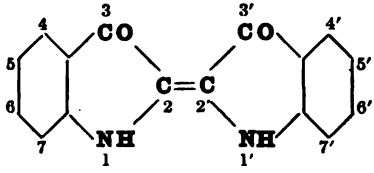
The term Indigoid is applied to the whole class of new dyes prepared from indigo and even from the derivatives. The various firms manufacturing these products have applied their

own special trade names to their own synthetic indigoid products, e.g., the Soc. pour l'ind. chim., Basle, calls its polyhalogenated indigo colors Ciba Dyes; while Meister, Lucius und Bürning, Höchst am Main, call their indigo products Helindone Dyes. Occasionally the term Helindone is also applied to derivatives of anthracene; this of course tends to confusion.

Associated with indigotine, which is the pure blue from the indigo plant, are other colored substances such as indirubin or indigo red, indigo yellow, indigo brown as well as indigo glutin and other impurities. These together with the thioindigo derivatives are the indigoid dyes in the narrow sense while the new dyes prepared from them by the action of the halogens are called ciba dyes, helindone dyes, etc., but as stated above the term indigoid is also applied to the whole family of dyes made from the relatives of indigo.

Halogenated Derivative of Indigo

Indigo itself is treated with chlorine and also with bromine; not in the presence of water; but dissolved in nitrobenzene, dichlorbenzene, glacial acetic acid, concentrated sulphuric acid or chlorsulphonic acid. To simplify the study of these new products, the indigo molecule is regarded as having its constituent atoms numbered as shown in the following structural formula:

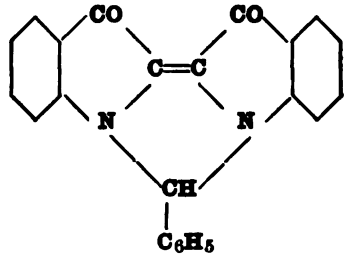


Indigo blue or Indigotine.

The mono and dihalogenated derivatives of indigo are of little value but the tri- and tetra-halogenated products are important. They exhibit very pure shades differing from the original indigo while retaining its fastness. The position taken by the substituting halogen has an important influence on the shade of the

dye. Ciba blue B and ciba blue 2B are the tri- and tetra-brom indigotine respectively.

Indian yellow 3G ciba was one of the first yellow vat dyes made from indigotine. Indigotine is changed into this yellow dye by heating with benzoyl chloride in excess. A brown powder melting at 108° is formed. Using nitrobenzene as a solvent with copper powder as a condensing agent, an intensely yellow dye—Indian yellow 3G ciba results. Its probable constitution is shown below:



Indian yellow 3G. ciba

Thus an exchange of the two imino hydrogens of a blue dye for a benzoyl group and the formation of a new pentatomic ring changes a blue dye to a yellow one.

The bromine derivative of this dye is known as ciba yellow G. Both are employed for vat-dyeing of wool, silk, and cotton. Indian yellow 3G ciba in the alkaline reduction vat gives a bluish red color to the liquid. It is of further interest since it may be dyed with indigo from the same vat producing green shades.

Frequently uneven shades are produced on attempting to dye a mixture of indigoid colors from the same vat because of the varied amounts of alkali and the special temperature required by each individual dye.

The most important derivatives are those containing the halogens. Chlorine and bromine are the ones employed. Two methods are available in implanting the halogen in the indigo molecule; either the halogen may act directly upon the indigo itself or it may act upon the initial constituents which are

later synthesized to form indigo. The halogenation is carried out in the absence of water and in one of the organic solvents mentioned above. The hydrogen atoms of the benzene rings are substituted by the halogens. Continued action of bromine directly upon indigo may cause the replacement of from one to six atoms of hydrogen.

Bromine enters first into position 5 forming a monobrom indigo; then into 5 5′ yielding a dibrom derivative and so on through the following series of positions: 55′7 to 55′77′ to 55′ 77′4′ to 55′77′4′4.

Direct bromination does not produce the 66′ compound. Curiously, however, this dibrom derivative was identified by Friedländer as the dye-stuff found in the shell-fish (murex brandaris) whence the ancients obtained the famous Tyrian purple. The probable reason for purple becoming the royal color was its high cost due to its variable source and small amount.

Though this dye is inaccessible by direct bromination, yet it has nevertheless been produced by an indirect method. In 4-bromo-2 amino benzoic acid was found a substance of which two molecules condensed to form a dibrom indigo with the bromine atoms in positions 66′.

The effect of the halogens upon indigo is to brighten the shade and render the new product even more resistant to bleaching than indigo itself. The increasing substitution of halogens is made at a sacrifice, however, for there is some loss in coloring power.

Homologues of indigo have been produced as well as halogen derivatives but they appear to possess no decided advantage. A dimethyl indigo 77′ is manufactured and sold as Indigo M. L. B. T. (M) and as Indigo pure B. A. S. F. (B). The shades of this dye are greener than indigo and they excel it in fastness to chlorine.

Amino Derivatives of Indigo

The entrance of amino groups into the indigo molecule changes the color from blue to brown. A brominated diamino indigo is made and sold as ciba brown R (S. C. I). Cotton

and wool may be dyed a reddish brown fast to light and washing but not to bleaching.

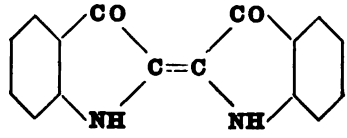
Naphthalene Indigo

Indigoid dyes have been prepared which contain the double ring nucleus in place of each of its single benzene nuclei of indigo. These products pass under the name of naphthalene indigo. They are green dyes instead of blue. The fugitive character of most of these renders them of little value. α and β naphthylamine are the compounds of naphthalene used as starting points for these dyes.

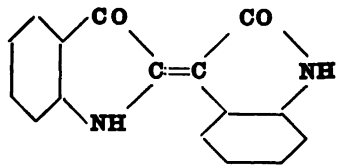
As exceptions to the comparatively slight value of these dyes in general, may be mentioned the brominated naphthalene indigos made from the β-compound which form valuable colors. Among these are Ciba green G (S. C. I), or Helindone green G. (M).

The naphthalene indigos sublime less easily than the simpler indigos and while Ciba green G will yield on heating reddish violet vapors, the most of them turn black and char without subliming.

Indirubin or indigo red is an isomer of indigo accompanying the indigo obtained from the plant. It does not occur in the purer indigo made from coal-tar sources. Indirubin may, however, be prepared by the condensation of isatin with indoxyl. It is valueless as a dye but it is interesting to note its molecular structure in comparison with its isomer indigo.



Indigo



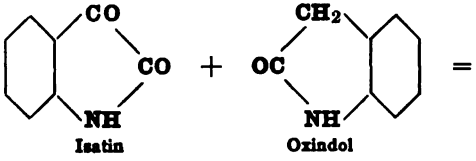
Indirubin

The unsymmetrical character of indirubin which renders it valueless as a dye is corrected by the action of bromine upon it.

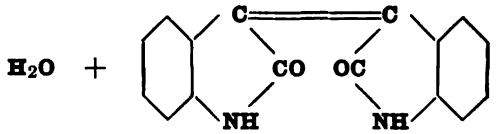
Indirubin when dissolved in nitrobenzene, treated with bromine and heated to 130° C. is changed into a commercial dye known as Ciba heliotrope. The bromination has produced a dye fast to washing.

Indirubin itself when present in the indigo vat is to a considerable extent transformed into indigo and some of it becomes fixed upon the wool; but the amount is small and the attachment feeble and liable to removal by washing.

Iso-indigotine. Wahl and Bayard have among the so-called indoginides which they have synthesized produced an isoindogenide of isatin. This is a true isomer also of indigotine. Its formula is symmetrical but a comparison with indigotine and indirubin will show the differences from each of these:

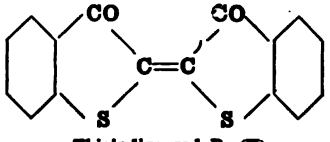


Isatin Oxindol



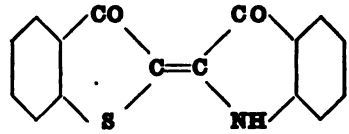
Iso-indigotine

Thioindigos are red vat-dyes which differ from indigotine in containing sulphur in place of one or more of the imino groups. If both imino groups of indigotine are replaced, a thioindigo red is produced as shown by the following formula:



Thioindigo red B. (K).

If only a single imino group is replaced by sulphur a thioindigo scarlet is produced as follows:



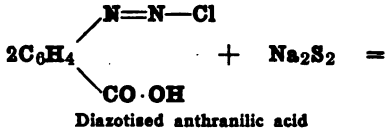
Thioindigo scarlet R. (K).

Thioindigo red B was discovered by Friedländer in 1895. Thioindigo dyes violet red shades from the usual alkaline vat. It may be prepared in a variety of ways. The following sequence will show its relation to an initial coal-tar product.

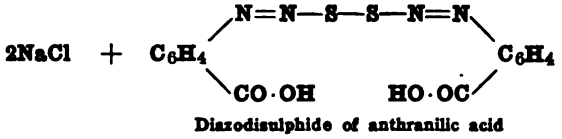
Toluene
↓
1. *o*-Nitrotoluene
↓
2. *o*-Aminotoluene
↓
3. Acetyl-*o*-amino toluene
↓
4. Acetyl-*o*-amino benzoic acid
↓
5. *o*-amino benzoic acid (anthranilic acid)
↓
6. Diazo-disulph anthranilic acid
↓
7. Dithio-salicylic acid
↓
8. Thiosalicylic acid
↓
9. Phenyl thio glycine-*o*-carboxylic acid
↓
10. Thio indigo red.

The methods for the first four steps may be found in the text books of organic chemistry. The fifth step may be carried out by allowing potassium permanganate to act upon *o*-amino toluene in a solution of magnesium sulphate and saponifying the product whereby anthranilic acid results.

The anthranilic acid is now diazotised and treated with a solution of sodium disulphide (Na_2S_2), made by dissolving the requisite amount of sulphur in sodium sulphide, according to the following reaction:

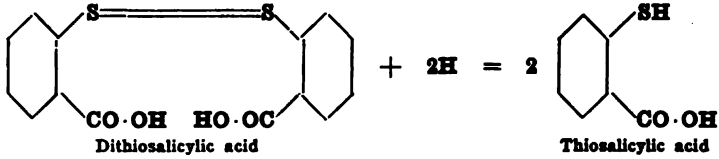


Diazotised anthranilic acid



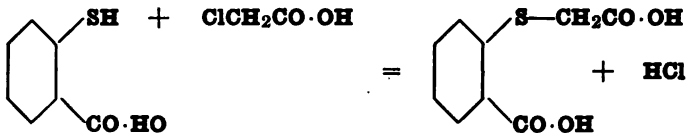
Diazodisulphide of anthranilic acid

This product is unstable and easily releases its nitrogen, forming dithiosalicylic acid. Reducing agents are then employed to break this up, converting it into thiosalicylic acid, as shown below:



Dithiosalicylic acid — Thiosalicylic acid

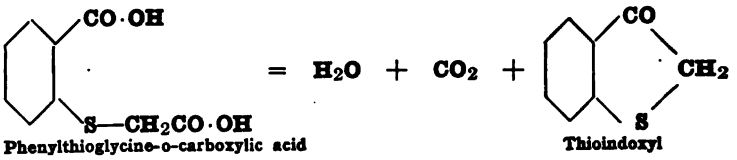
Monochlor acetic acid is allowed to act upon its thiosalicylic acid and converts it into phenylthioglycine-*o*-carboxylic acid.



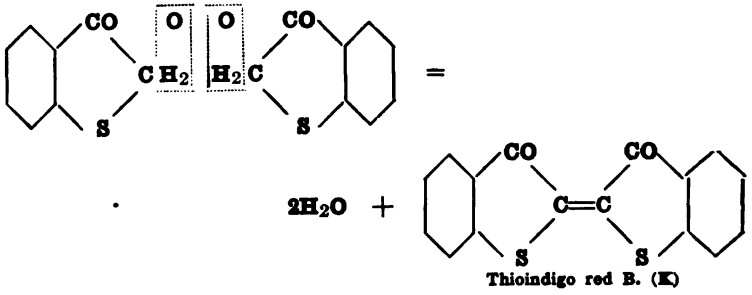
Thiosalicylic acid — Phenylthioglycine-o-carboxylic acid

Fusion of this substance with alkalies and oxidizing the product dissolved in water by ferric chloride, potassium dichromate or even by a current of air yields Thioindigo red B.

What takes place during the fusion and subsequently is represented below:

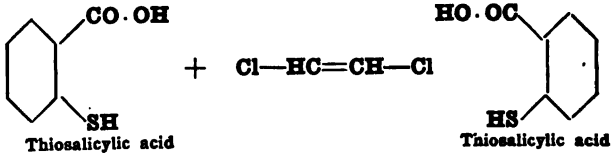


Phenylthioglycine-o-carboxylic acid — Thioindoxyl



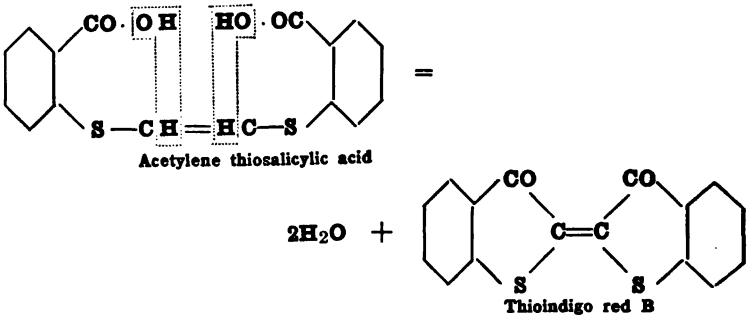
Thioindigo red B. (K)

As many processes have been carried out for the synthesis of ordinary indigo, so a variety of methods have been used to obtain Thioindigo red B. One such process employs acetylene dichloride which condenses with two molecules of thiosalicylic acid as follows:



Thiosalicylic acid — Thiosalicylic acid

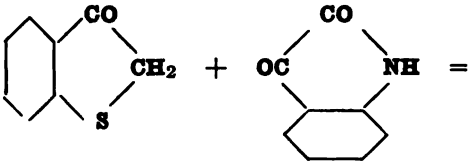
By dehydration of the product of the above reaction Thioindigo red B results.



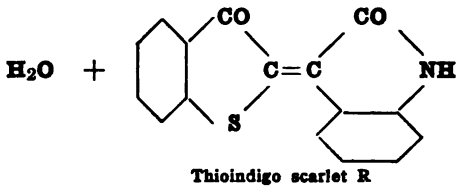
Acetylene thiosalicylic acid

Thioindigo red B

Thioindigo scarlet R. The indigoid dye, possessing but one sulphur atom in its molecule, exhibits a yellower shade of red and is known as Thioindigo scarlet R. It is formed by the condensation of isatin with oxythionaphthen—a method which reveals the molecular structure of this dye, as shown below:



Oxythionaphthen. Isatin

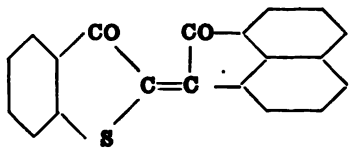


Thioindigo scarlet R

Its formula will be observed as unsymmetrical as well as containing but a single atom of sulphur. It is a vat dye producing brilliant scarlet shades upon cotton.

Both of these thioindigo dyes have become the starting points for a series of other dyes by being subjected to chlorination or bromination whereby valuable ciba (S. C. I.) and Helindone (M) have been manufactured and placed on the market.

Ciba scarlet G (S. C. I.). Acenaphthen, a constituent of coal-tar which had previously no commercial use, is brought to an important application in the manufacture of this dye. As an indigo derivative, it shows a marked contrast to indigo in the structure of its molecule.

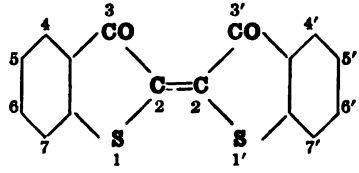


Ciba scarlet G

This dye results from a condensation of acenaphthoquinone with oxythionaphthen. It is a valuable vat dye fast to almost all influences.

While the derivatives of indigotine are not very different in color, the derivatives of thioindigo vary greatly, yielding colors covering nearly the whole range of the spectrum. Thus the substitution of sulphur for an imino group increases the scope of color formation to a remarkable degree.

Thioindigo red B may be substituted in many different positions and the influence of the substituted groups may be observed in the following formulas:



Thioindigo red B. Positions indexed

The following scheme shows the effect of substituting the hydrogen atoms in various positions in Thioindigo red B with different atoms or groups of atoms.

	Substituent		Position		Color
Thioindigo red B	OCH_3	for H	(6 : 6′)	→	Orange red
	OCH_3	for H	(4 : 4′)	→	Blue violet
	OC_2H_5	for H	(6 : 6′)	→	Bright orange
	OC_2H_5	for H	(5 : 5′)	→	Dark violet
	NH_2	for H	(6 : 6′)	→	Orange brown
	NH_2	for H	(4 : 4′)	→	Greenish black
	NH_2	for H	(7 : 7′)	→	Gray.

Below is given a list of derivatives of thioindigo appearing in commerce.

Trade Name.	Substituting Groups.	Constitution.
Thioindigo red B.G. Helindone red B.	Chlorine	5 : 5′ Dichlorthioindigo
Ciba red B.	Chlorine	6 : 6′ Dichlorthioindigo
Helindone red 3B. Thioindigo red 3B.	Chlorine and methyl	5 : 5′ Dichlor-6 : 6′-dimethyl-thioindigo

Trade Name.	Substituting Groups.	Constitution.
Helindone fast scarlet R.	Chlorine and ethoxy	5 : 5′ Dichlor-6 : 6′-diethy thioindigo
Helindone gray B.R.	Chlorine and amino	Dichlor-7 : 7′ diaminothioindigo
Thioindigo violet 2B. Helindone violet 2B.	Chlorine, methyl and methoxy	Dichlor-dimethyl-dimethoxy-thioindigo
Ciba Bordeaux B.	Bromine	5 : 5′ Dibromthioindigo.
Thioindigo pink B.N. Helindone pink B.N.	Bromine and methyl	6 : 6′ Dibrom-dimethyl-thioindigo
Helindone orange D.	Bromine and amino	Dibrom-6 : 6′-diamino-thioindigo
Thioindigo orange R. Helindone orange R.	Ethoxy	6 : 6′ Diethyoxy-thioindigo
Thioindigo scarlet S. Helindone scarlet S.	Thioxyl	6 : 6′ Diethoxyl thioindigo
Thioindigo gray 2B. Helindone gray 2B.	Amino	7 : 7′ Diamino-thioindigo

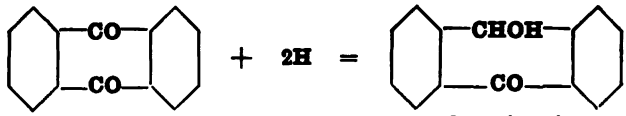
Anthraquinone Vat Dyes

Anthraquinone vat dyes are used chiefly upon cotton; the amount of alkali used in the vat precludes the application to wool and silk in general, although wool has at times been rendered immune to the action of the large percentage of alkali by treatment with formaldehyde.

Anthracene is a product obtained directly from coal-tar. By oxidation it produces anthraquinone. This by further treatment is converted into alizarin (1 : 2 dioxyanthraquinone) which is the source of Turkey Red.

But alizarin was not a vat dye nor was Turkey red a vat color.

To develop the property of a vat dye from anthraquinone, an alkaline reducing agent must be used whence nascent hydrogen developed a hydroxyl group from one of the ketone groups forming a product called oxyanthranol as shown below:

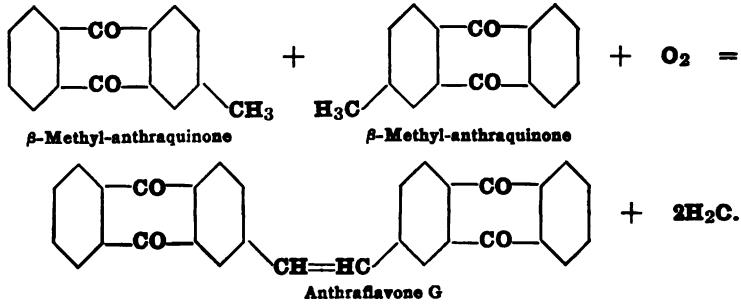


Anthraquinone Oxyanthranol

In an alkaline solution oxyanthranol dissolves by virtue of its hydroxyl group, and forms a solution of blood-red color. Exposure to air causes its oxidation back to the colorless and insoluble anthraquinone. Now it is not the color of the vat itself but the product of oxidation remaining in the fibre which is the permanent dye.

Accordingly oxyanthraquinol has no tinctorial properties. The color properties of anthraquinone or of its simpler derivatives are not marked enough to give them the rank of dyes. To produce true vat-dyes from anthraquinone, it seems necessary to bring about greater complexity in the molecular structure of whatever derivative of anthraquinone is to become a dye. In addition to the ketone groups, nitrogen, sulphur or other atoms or groups must be present.

Anthraflavone G (B). One of the simplest anthraquinone derivatives which is at the same time a valuable vat dye is known as anthraflavone G. This is made from β-methyl-anthraquinone by heating it with alcoholic potash to 150° C. to 170° C. whereby hydrogen is oxidized away from the methyl groups causing two molecules to combine by the union of the impoverished methyl groups as shown below:



In the alkaline reducing vat anthraflavone G appears as a dark reddish brown solution from which cotton is dyed a fast greenish yellow.

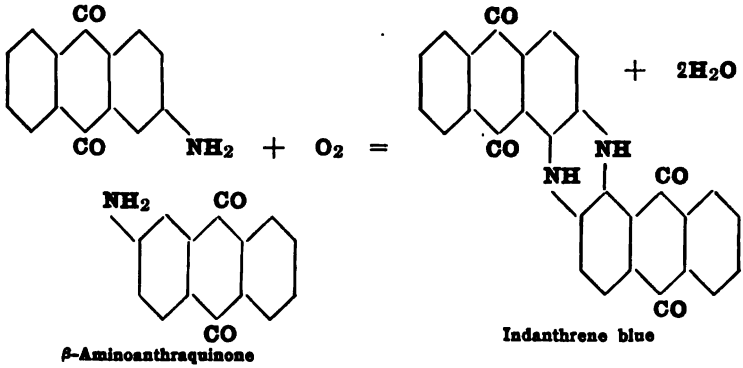
It consists of a double molecule of anthraquinone joined by an acetylene residue and may be called symmetrical di-anthraquinone acetylene.

Indanthrene Blue R was discovered by R. Bohn in 1901 at the Badische Anilin und Soda Fabrik. It was the first of the vat dyes to be obtained from anthracene. The process of manufacture was comparatively simple but it was a difficult matter to explain what took place during its formation. The method consisted in heating β-aminoanthraquinone with caustic potash to 200° C. to 300° C. The resulting mass was then dissolved in boiling water agitated by blowing a current of air through it; then the dye was precipitated in crystalline form.

What actually takes place has been the subject of study for half a dozen years by at least six investigators. It has now been determined that each of two molecules of β-aminoanthraquinone loses a hydrogen atom from an amino group and then a hydrogen from a neighboring carbon atom. A double union thus results forming the complex molecule of the dye.

$$2C_{14}H_9O_2N = C_{28}H_{14}O_4N_2 + 2H_2$$

The reaction is not so simple as this, for alizarin is also formed during the process. The hydrogen atoms are removed by oxidation and the structural union which follows is shown below:



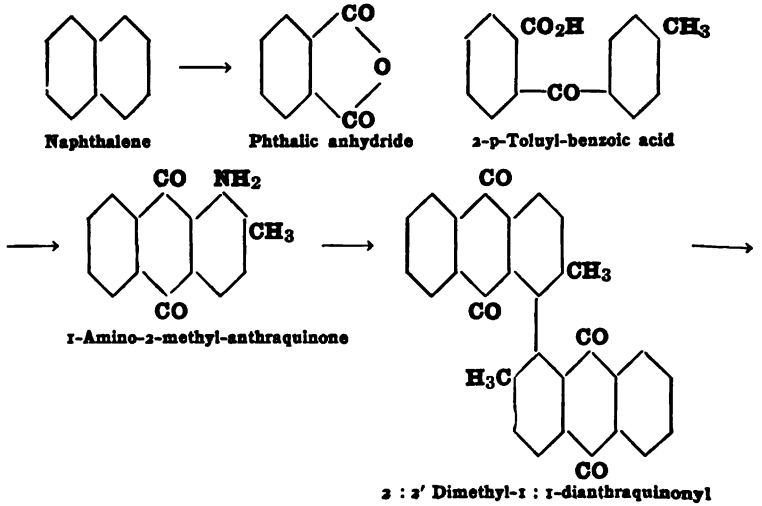
This dye appears in commerce as Indanthrene R S (B. A. S. F.) The trade name " Indanthrene " is now applied to all the anthraquinone derivatives of the Badische Company. Indanthrene blue R S (B) appears in beautiful blue coppery crystals which are insoluble in water, hydrochloric acid and

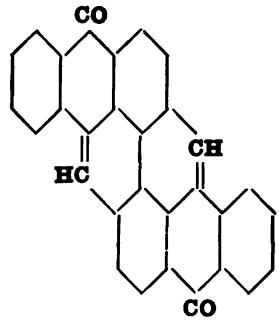
caustic soda. In concentrated sulphuric acid it forms a brown solution. It dyes cotton from an alkaline reducing vat bright blue shades which are fast to light washing acids and alkalis but not to chlorine. In its fastness to light it is superior to indigo.

Indanthrene R. C. As indanthrene blue R. S. is not resistant to chlorine, it was made so by introducing halogens into the dye molecule. The removal of one hydrogen atom and the entrance of one bromine atom accomplishes this result. This monobrom derivative is the dye Indanthrene blue R. C. Indanthrene blue G. C. is a dibrom derivative; Indanthrene blue G.C.D. and E.E. and Algol blue C.F. are chlorine derivatives of Indanthrene blue R. S.

Indanthrene gold orange G. is a derivative of anthraquinone and hence of anthracene; but neither of these substances forms the starting point for its formation. Naphthalene and toluene are the initial substances employed and the genetic relation they sustain to the dye itself is shown in the following sequence:

Naphthalene → Phthalic Anhydride → *p*-Toluylbenzoic
Toluene ——————↑
acid → 2-Methylanthraquinone → 2 : 2′ Dimethyl 1 : 1′
dianthraquinonyl → Indanthrene gold orange G.





Indanthrene gold orange G. (B)

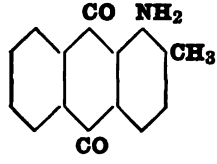
Indanthrene Gold Orange R. (B) is a chlorine derivative of the orange G.

Indanthrene Scarlet G. (B) is a bromine derivative of the orange G. The bromination is carried out in a nitrobenzene solution.

The processes for Indanthrene gold orange G. are in detail as follows:

2-Methylanthraquinone crystallizes in pale yellow needles melting at 177°, and is soluble in acetic acid or benzene but sparingly so in ether.

1-Amino-methylanthraquinone



2 parts 2-Methylanthraquinone
12–14 parts Sulphuric acid
1 part Potassium nitrate (or the equivalent amount of sodium nitrate).

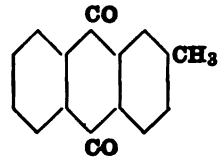
The methylanthraquinone is dissolved in the sulphuric acid and the potassium nitrate is added gradually, the whole being cooled. A greenish yellow crystalline mass is obtained which, after twenty-four hours, is poured into water. The yellow

product is filtered off, washed, and boiled with alcohol until the extract is pale yellow. The product is 1-Nitro-2-methylanthraquinone. When it is crystallized from glacial acetic acid, it melts at 269–270°; it is sparingly soluble in alcohol, ether, benzene, chloroform or acetic acid, but readily so in xylene, nitrobenzene, or aniline (Römer and Link, Ber., 1883, 16, 695).

For the subsequent reduction, 1 part of the nitro-compound is boiled with 3½ parts of crystallized sodium sulphide and 20 parts of water for an hour (Römer and Link used stannous hydroxide).

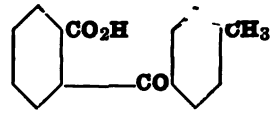
The processes involved in making indanthrene gold orange G. starting from phthalic anhydride is as follows:

2-Methylanthraquinone from phthalic anhydride.



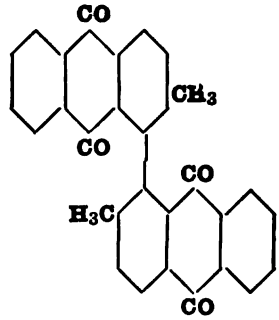
50 grams Phthalic anhydride.
200 grams Toluene.
100 grams Aluminum chloride, pulverized.

The phthalic anhydride and toluene are mixed and the aluminum chloride added. Hydrogen chloride is evolved and the moisture becomes warm. After ten hours water is added and the excess of toluene is removed by a steam distillation: the aqueous solution is poured off (the small amount of phthalic acid may be recovered by acidifying). The remaining cake is rendered alkaline by sodium carbonate, steam is passed in for four to five hours, the whole filtered, and the filtrate acidified, whereby



2-p-Toluylbenzoic acid

2-*p*-toluyl benzoic acid (m. p. 146°) is precipitated (79 grams) in a yield which is 97 per cent of the theoretical. The acid is now dissolved in 9 parts of fuming sulphuric acid (20 per cent of SO_3) and heated on the water bath for 1½ hours. On pouring into water 2-methyl anthraquinone is obtained and is filtered off and dried. (Heller and Schülla, Ber., 1908, 41), and, if necessary, the amino-compound is crystallized from glacial acetic acid (Scholl and Holdermann, Ber., 1907, 40, 1696), 1-Amino-2-methylanthraquinone melts at 202°. It is insoluble in water, but readily so in alcohol, ether, benzene, or acetic acid. It is converted into 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl as described below:



2 : 2′-Dimethyl-1 : 1′-dianthraquinonyl

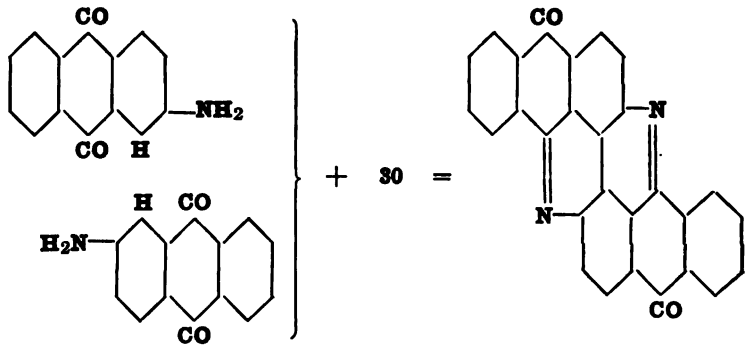
20 parts 1-Amino-2-methylanthraquinone.
250 parts Sulphuric acid (97 per cent).
8 parts Solid sodium nitrite.

To the solution of the first substance in the sulphuric acid, the powdered sodium nitrite is added gradually at the ordinary temperature. When the diazotisation is complete, the product is poured on 500 parts of ice; and after three hours the diazonium sulphate is filtered off, washed successively with a little cold water, alcohol, and ether and dried in the air. Ten parts are then stirred with 60 to 80 parts of acetic anhydride and 2 parts of copper powder (" copper bronze ") are added. Nitrogen is evolved and a violet-solution is obtained from which after a few hours, a yellowish white precipitate separates out.

This is warmed on the water bath, filtered, and the residue suspended in hot water to destroy acetic anhydride; then treated with dilute nitric acid to dissolve copper, and filtered off. 2 : 2′-Dimethyl 1 : 1′-dianthraquinonyl melts at 366–367° and is readily soluble in boiling aniline or nitrobenzene, but sparingly soluble in boiling xylene. The sulphuric acid solution is yellow.

Heat with or without a dehydrating agent converts it into indanthrene gold orange.

Indanthrene yellow G. is an interesting example of a yellow dye formed from the same initial substances employed for indanthrene blue R. In making the latter, β-aminoanthraquinone was heated with caustic potash and an oxidizing agent: air or potassium nitrate. The process is carried on as when producing the yellow dye except that the temperature is much higher. This causes a union β-aminoanthraquinone molecules in a different manner as may be seen by comparing the following formula with that of indanthrene blue R.



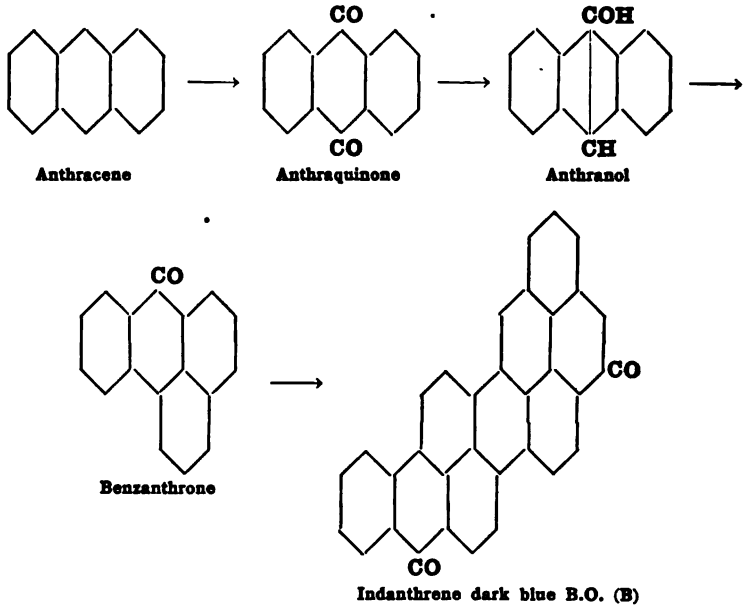
β-Aminoanthraquinone — Indanthrene yellow G

By dissolving β-aminoanthraquinone in nitrobenzene and treating the solution with antimony pentachloride the same yellow dye may be obtained.

Indanthrene Dark Blue B. O. The following sequence of substances reveals the relation this dye and the parent substance anthracene.

Anthracene → Anthraquinone → Anthranol → Benzanthrone → Indanthrene Dark Blue B. O. (B).

Fusion of benzanthrone with caustic alkali produces the dye: the progressive steps from anthracene are shown below:



Preparation of Anthranol. Ten grams of anthraquinone are boiled with 400–500 grams of glacial acetic acid and 25 grams of tin added. About 10 cc. of fuming hydrachloric acid are poured in and the yellow color changes to brown, which, however, soon disappears. Small quantities of hydrochloric acid are added to the boiling liquid as long as the color changes to brown and in order to maintain a constant production of hydrogen. The process is finished after fifteen minutes, the end of the reaction being shown by a sample, on cooling, remaining clear and giving no precipitate of anthraquinone. The whole is then poured into water and acidified with hydrochloric acid, when anthranol is obtained in a yield of more than 80 per cent of the theoretical. It melts and decomposes at 163–

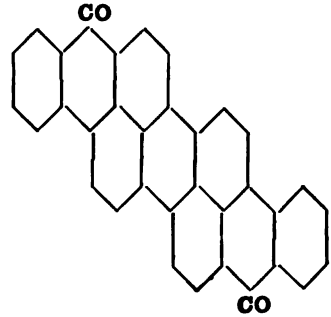
170° C. and can be obtained pure by recrystallization from glacial acetic acid.

Preparation of Benzanthrone. Ten parts of anthranol are dissolved or suspended in 150 parts of sulphuric acid (62° Bé) and 10 parts of glycerol are added. The mixture is carefully warmed; at 120° C. it begins to turn red and sulphur dioxide is evolved. When the reaction is complete (after four hours at 120° C.), the cooled mass is poured into water, and the product separates in olive green flocks which are collected, washed, boiled for half an hour with thirteen times the quantity of sodium hydroxide solution (1 per cent) pressed and dried. The crude substance is an olive green powder insoluble in dilute acids or alkalis, but dissolves in sulphuric acid with a reddish brown color and deep orange fluorescence. It crystallizes from alcohol in pale yellow needles melting at 170° C.

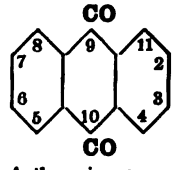
The dye yields reddish-violet shades on cotton which become blue by washing.

Indanthrene green B. (B.) is obtained by the nitration of indanthrene dark blue B.O. It becomes itself the source of another dye because cotton dyed green with this color may be changed by oxidizing agents to a fast black called indanthrene black B. (B).

Indanthrene violet R. is an isomer of indanthrene dark blue B.O. In the place of benzanthrone which is fused with caustic potash for the latter, a halogen derivative of benzanthrone is melted with caustic potash thereby producing the isomeric form of the following structure:



Indanthrene violet R. extra (B)



Anthraquinone
Numbered positions

Algol W.G. The Baeyer-Farben-Fabrik found that simpler condensations than those where two or more anthraquinone molecules condense to produce a highly complex dye molecules. Indeed so simple a substance as benzoylchloride would condense amino-anthraquinones and confer upon the product the property of a vat dye, e.g., α-aminoanthraquinone reacts with benxoylchloride to form a vat dye which gives rich yellow shades on cotton under the name of algol W.G. It is of interest that a compound of so relatively simple structure should exhibit properties possessed by those of more highly complex structure. Many similar examples are known where dibenzoyl derivatives of diamino-anthraquinone and dibenzoyl derivatives of oxydiaminoanthraquinones and further succinyl and acyl derivatives rise to the rank of vat dyes. In the following series:

Benzoyl-1-aminoanthraquinone	is Algol yellow W.G.
Succinyl-(1-aminoanthraquinone)$_2$	is Algol yellow 3G.
Dibenzoyl-1 : 5-diaminoanthraquinone	} is Algol yellow R.
Dibenzoyl-1 : 4-diaminoanthraquinone	} is Algol red 5G.
Dibenzoyl-1 : 5-diamino-8-hydroxyanthraquinone	} is Algol red R. extra.
Benzoyl-4-amino-1-hydroxyanthraquinone	} is Algol pink R.
Benzoyl-1-amino-4-methoxyanthraquinone	} is Algol scarlet G.
Dibenzoyl-diamino-anthrarufin	is Algol blue 3R.
Benzoyl-1 : 2 : 4-triaminoanthraquinone	} is Algol brilliant orange F.R.

1 : 5 Dimenzoyldiamino-4-hydroxanthraquinone	} is Algol brilliant red 2B.
Succinyl-diamino-anthraquinone	is Algol brilliant violet R.
Chlorsulphuric acid upon dibenzoyldiamino-anthraquinone	} is Algol olive R.
Benzoylamino-4 : 5 : 8-trihydroxyanthraquinone	} is Algol violet B.

Sulphur Vat Dyes

The dyes of this class should not be confined with the ordinary so-called sulphur dyes. These vat dyes are obtained from the initial substances, anthracene or derivatives of anthracene, or from indophenol of carbazol or its derivatives. They are heated to a high temperature with sulphur alone, or with alkali polysulphides, or other sulphur compounds, e.g. sulphur chloride.

The resulting products are true vat dyes being insoluble in sodium sulphide but reduced to leuco-compounds which are made soluble by the action of sodium hydrosulphite.

These dyes appear in commerce under the names: Cibanone dyes (Soc. pour l'ind. chim. Basle); Hydron Dyes (Cassella); Indanthrene Dyes (Badische Anilin und Soda Fabrik), etc. The name Hydron includes also other than the sulphur vat colors.

Sulphur Anthracene Derivatives

Indanthrene olive G. is one of the simplest of this class of dyes. It is formed by heating anthracene 96 to 98 per cent pure with three parts of sulphur to a temperature of 250° C. until the odor of the evolved hydrogen sulphide disappears.

The vat containing the leuco form of this dye is colored dark violet and from it are dyed olive shades which show fastness to both light and washing.

Hydron olive G (C.) is a dye of a nature probably similar to the above. Instead of sulphur, sulphur chloride is employed upon anthracene and at a high temperature.

Cibanone blue 3G (S.C.I.) is the result produced by heating 2-methylbenzanthron with sulphur to a high temperature.

Cibanone black B (S.C.I.), cibanone black 2B and cibanone green B. are probably produced by varied treatment of 2-methylbenzanthrone with sulphur at a high temperature.

It is of interest to note here that apparently worthless products are sometimes susceptible to an after treatment which renders them valuable. For example, 2-methylbenzanthrone containing a substituted hydrogen in its methyl group may produce, on melting with sulphur and heating, substances of dull or valueless shades. However, oxidation of these same compounds with sodium hypochlorite will change them into bright orange dyes.

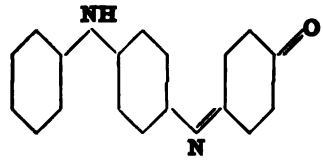
Cibanone yellow R. (S.C.I.) is obtained by fusion of monochlor-methylanthraquinone with sulphur and subsequent oxidation with sodium hypochlorite. Cibanone orange R. originated from the dichlormethyl anthraquinone and heat treatment with sulphur and oxidation with sodium hypochlorite.

When amino and diamino groups are present in 2-methylanthraquinone, the fusion with sulphur gives rise to colors varying from yellow to violet brown. Cibanone brown is supposed to be prepared from the monoamino-2-methylanthraquinone.

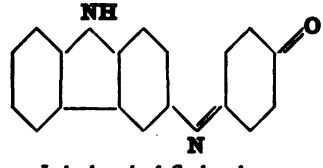
Sulphur Vat Dyes from Indophenol

The treatment of many organic compounds with sodium polysulphide, principally Na_2S_4, produces chiefly dyes known as sulphur dyes. The employment of free sulphur with the polysulphide yielding a more highly sulphurized polysulphide Na_2S_7 or Na_2S_8 (?) produces new dyes which are not soluble in sodium polysulphide. These are reduced to leuco bodies which do dissolve in the vat and show the nature of genuine vat dyes.

Carbazol was found by L. Haas to form a condensation product with nitrosophenol in solution in sulphuric acid. The result was an indophenol corresponding to the indophenol of diphenylamine that is produced in a similar way.



Indophenol of Diphenylamine



Indophenol of Carbazol

Hydron blue R. (C.). By heating this indophenol of carbazol with sulphur and sodium sulphide a blue sulphur vat dye called hydron blue R. (C.) is produced.

Indocarbon S. (C.) is formed by adding copper sulphate to the hydron blue R. melt, when a product is obtained which dyes cotton shades of black.

If a more intensive treatment with sodium polysulphide is given to indophenol-carbazol or to its acyl or alkyl derivatives or to the product resulting from condensing dinitrochlor benzene with leuco indophenol carbazol, dyes of a different nature appear and they are brought into commerce under the names hydron blue R.G.B. and hydron blue black.

Hydron yellow G. is not a sulphur vat dye but it results from the action of some dehydrating agent, e.g., sulphuric acid and upon dinaphthaloyl carbazol, causing a condensation.

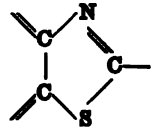
Hydron violet B. resembles the dyes of the indigoid class.

It is stated by Erban that shades greener and redder than those of indigo have been obtained in the dyes hydron blue G. and R. and that they excel even indigo in their resistance to boiling, washing and bleaching.

CHAPTER XX

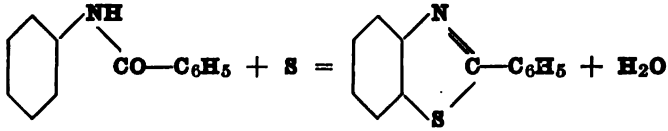
THIAZOL DYES

THE name thiazol implies the presence of sulphur and nitrogen (θεῖον: sulphur and azote; nitrogen). It also implies the presence of the so-called "thiazol ring." This ring consists of three atoms of carbon, one of sulphur and one of nitrogen as shown below:



Thiazol ring

Hoffman obtained the first member of this group of dyes by fusing benzanilide with sulphur forming phenylbenzthiazol. Two atoms of hydrogen and one of oxygen split off as a molecule of water leaving the sulphur to close the gap and form the thiazol ring as follows:



Benzanilide Phenylbenzthiazol

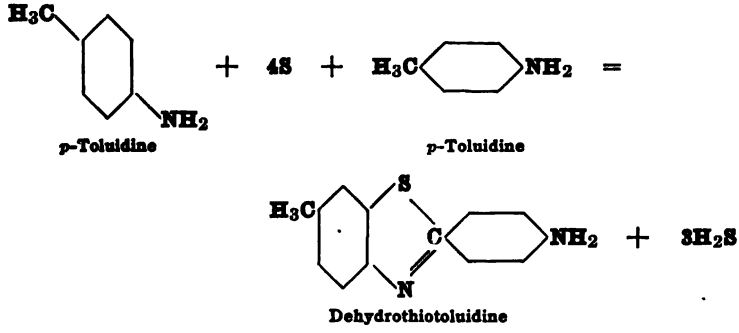
As a matter of fact, phenylbenzthiazol and its simplest derivatives are colorless; yet it is itself a chromogen; for on introducing in the para position to the single carbon atom of the thiazol ring, products of a slightly yellow color result.

Primuline. The most important thiazol derivatives are made by fusing an intimate mixture of *p*-toluidine or its homologues with sulphur. The reaction of these substances was discovered in 1887 by Green and the manufacture of primuline was begun at once near London by Brooke, Simpson and Spiller. Though the process was not patented, several patents have been granted relating chiefly to the separation and purification of the products of the fusion.

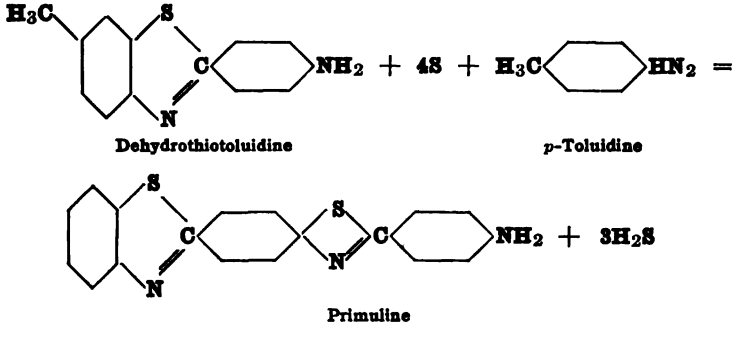
When *p*-toluidine is intimately mixed with sulphur and heated to 200° hydrogen sulphide is evolved. This shows a removal of hydrogen from those parts of the molecules where subsequent union with sulphur is made possible.

The fusion with sulphur yields two products, dehydrothiotoluidine and primuline. The relative amounts of these products depends upon the length of the time of fusion, the temperature, and the amount of sulphur employed.

Dehydrothiotoluidine is the chief product when the substances are mixed in the proportion of two molecules of *p*-toluidine and four atoms of sulphur; as shown in the following reaction:



If the fusion is continued for a longer time or if made at a higher temperature, sulphur works to unite a molecule of *p*-toluidine with the dehydrothiotoluidine already formed to produce primuline as represented below:



The chemical constitution shown above is the result of the labors of Jacobson, Gatterman, Anschutz, Schultz, and others.

It is of interest to note the preparation on a commercial scale.

Manufacture of Primuline. There are several methods of preparing primuline on a commercial scale of which the following gives full details:

The "primuline melt" is made in an enamelled iron pot of about 200 gallons capacity which is set in brick work and provided with an iron enamelled agitator. The lid of the pot also carries a thermometer tube and a hole for charging and emptying which is closed by a flange. Connected with the lid is a cast-iron pipe (preferably enamelled) of 8–10 inches internal diameter and about 40–50 feet long. This pipe is inclined upward and serves as an air cooler to condense and return to the pot the *p*-toluidine which is carried off as a vapor by the hydrogen sulphide. The whole or a part of the pipe can, if necessary, be cooled by a spray of water. From the further end a smaller pipe (2 inches in diameter) carries the gas which should then be quite cold, to an iron box, in which a little *p*-toluidine collects, and thence it passes to the furnace, where it is burnt under the pot, which it serves to heat, the excess being led away by a branch pipe to be burnt in the chimney.

The pot is charged with 1000 pounds of *p*-toluidine and 670 pounds of sulphur. This is heated to the boiling-point for several hours, the temperature slowly rising as the reaction proceeds. The evolution of hydrogen sulphide commences at about 170° and is complete when the temperature reaches 270°. The agitator is then stopped and the hot fluid is transferred from the pot under air pressure by means of a pipe inserted through the charging hole. After cooling and solidifying, the product is reduced to pounds by means of a disintegrator. The yield is about 1.125 pounds.

The sulphonation is performed in an enamelled iron-jacketed pan of 220 gallons capacity provided with cooling pipes through which cold water can be circulated. The contents of the pan can be rapidly stirred by means of an agitator, the blades of which pass between the loops of the cooling pipes. The ground

melt (400 pounds) is dissolved with rapid agitation in 1000 pounds of 100 per cent sulphuric acid (final temperature about 90°). There is then added slowly, while the mixture is kept rapidly agitated and well cooled, 800–900 pounds of fuming sulphuric acid (containing 70 per cent sulphur trioxide). The temperature is not allowed to rise above 40°, and the operation lasts about 6 hours. (The same result is not obtained by initially employing, for example, 1.860 pounds of fuming sulphuric acid containing 32 of sulphur trioxide.) The sulphonation is complete when a small sample precipitated in water dissolves to a perfectly clear solution in boiling dilute ammonia. The mixture is then blown out of the pot by compressed air through the hollow spindle of the agitator, and is run by means of a lead pipe into a wooden vat containing about 3000 gallons of cold water in which the dehydrothiotoluidine and primuline sulphonic acids are thrown down as a voluminous orange yellow precipitate. This is filtered off through a wooden filter press, in which it is thoroughly washed with water until all mineral acid is removed.

In order to effect the separation of the dehydrothiotoluidine-sulphonic acid from the primuline-sulphonic acid, the sparing solubility of the ammonium salt of the former is made use of. The mixed sulphonic acids, in the form of the wet press cake, are stirred up with concentrated ammonia in a wrought iron vessel provided with an agitator. The primuline dissolves while the dehydrothiotoluidine sulphonate separates out as a silky crystalline precipitate. The mixture is transferred to a suction filter and the precipitate is washed with a little water until nearly white. On adding common salt to the filtrate, the primuline is thrown down as a dark yellow granular precipitate, which, after drying, is ground with sufficient common salt to bring it to standard strength. A small quantity which remains in the filtrate is recovered by adding the latter to the acid precipitating vat. The yield under the best conditions amounts to 530–560 pounds of ammonium dehydrothiotoluidine sulphonate, and 1700–1800 pounds of standard primuline from 1000 pounds of *p*-toluidine (Green, "Dictionary of Applied Chemistry," Thorpe, 1913, IV, 386).

Ingrain Colors from Primuline

Aside from the primrose yellow produced directly upon unmordanted cotton from an alkaline or neutral bath, other so-called ingrain colors are obtained by the use of primuline.

These colors include red, brown, orange, maroon, crimson, etc., by diazotisation of primuline upon the fibre and combining with various second component substances. Primuline is dyed upon cotton which is treated with nitrous acid and then with a phenol or amine with such results as are given below:

Primuline diazotised and combined with:

Phenol yields ingrain yellow.
Resorcinol yields ingrain orange.
m-Phenylenediamine yields ingrain brown.
β-Naphthol yields ingrain red.
α-Naphthol-sulpho-acid N.W. yields ingrain crimson.
β-Naphthol-di-sulpho-acid R. yields ingrain maroon.

An interesting photographic application of primuline has been carried out as follows: Diazotised primuline is very sensitive to light and is destroyed by it. By exposing the fabric dyed with primuline and diazotised and exposed to light under a positive design, the diazo-primuline is quickly destroyed in the exposed portions and then on treating with a phenol or amine, the protected parts alone respond to development producing a design in color.

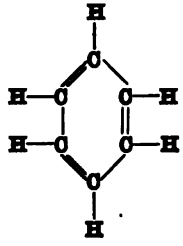
CHAPTER XXI

EXPERIMENTAL WORK

In the following experiments the benzene molecule with its six carbon and six hydrogen atoms is represented by the plain hexagon below:

C_6H_6

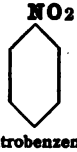
Benzene



Benzene

Benzene
Abbreviated formula

If one of the hydrogens is replaced, e.g., by a nitro group ($—NO_2$), then the abbreviated formula stands for the benzene molecule minus the hydrogen which has been replaced, i.e., C_6H_5.



Nitrobenzene

Experiment 1

Properties of Benzene. Pour a few drops of alcohol upon a flat piece of board and an equal number of drops of benzene near by; then ignite both and note the character of the two flames. To one cc. of alcohol add two drops of

benzene; pour out the mixture upon the board and ignite it. How does the flame compare with that of pure alcohol or pure benzene?

The burning of alcohol (containing 52.2 per cent of carbon):

$$C_2H_6O + 3O_2 = 3H_2O + 2CO_2$$

The burning of benzene (containing 92.3 per cent of carbon):

$$2C_6H_6 + 3O_2 = 12C + 6H_2O$$

The oxygen of the air (about 20 per cent) is sufficient to burn both the hydrogen and the carbon of the vapor of alcohol; but it is sufficient to burn the hydrogen and only a part of the carbon of the vapor of the benzene. The unburnt carbon passes off as dense black smoke.

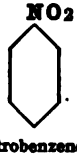
To 1 cc. of benzene in a test-tube, add an equal quantity of ether. Do the liquids mingle or separate on shaking?

To a test-tube containing a few drops of oil or a piece of tallow as large as a pea, add a few cubic centimeters of benzene and note the effect of continuous shaking.

Experiment 2

Nitrobenzene from Benzene.

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$



Nitrobenzene

To 150 grams (or 83 cc.) of concentrated sulphuric acid in a one-half liter flask add, little by little, with frequent rotary shaking, 100 grams (or 71 cc.) of concentrated nitric acid of specific gravity 1.4.

After the mixture has been cooled to the temperature of the room by water running from a tap over the flask or by immersing it in water, add in small portions 50 grams of benzene, shaking frequently, so as to make the liquid acquire a rotary motion in the flask.

The temperature should be kept under 50° to 60° C.; should it rise higher, interrupt the process and immerse the flask for a short time in water.

After all the benzene has been added, attach a vertical glass tube to the perforated stopper to serve as an air condenser. It is then heated in a water-bath for an hour at 60°, the thermometer in the water. The following reaction has taken place:

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

The liquid is then well cooled and poured into a separating funnel, where it is allowed to stand a few minutes while it separates into two layers. The lower contains the spent sulphuric acid and the excess of nitric acid, and it is separated from the upper layer of nitrobenzene by slowly opening the stopcock and allowing it to run out into a beaker.

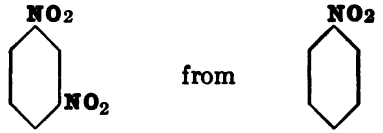
The nitrobenzene is then vigorously shaken several times with water; since the nitrobenzene is heavier than water, it will now be the lower layer. This must be kept in mind or the wrong layer may be thrown away.

When thoroughly washed by shaking several times with fresh portions of water and separating each time from the water, it is poured into a dry flask and warmed on a water-bath with granulated calcium chloride until the turbid liquid becomes clear. It is then poured carefully off from the calcium chloride and purified by distilling from a fractionating flask attached to a long air condenser.

Nitrobenzene boils at 206–207°. The yield from 50 grams of benzene is 60–70 grams.

EXPERIMENT 3

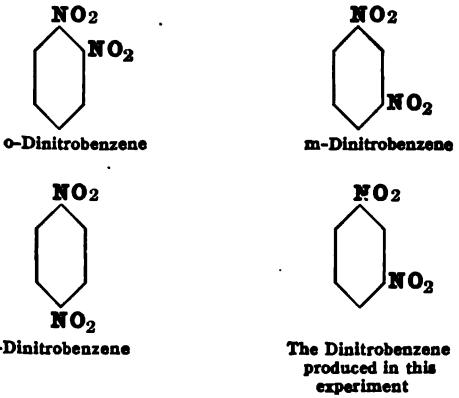
Dinitrobenzene from Nitrobenzene.



m-Dinitrobenzene — Nitrobenzene

In the previous experiment the temperature is kept under 60°, to avoid converting a large portion of the benzene into dinitrobenzene, which it is the object of the present experiment to produce exclusively; hence a higher temperature will be necessary.

Formulas of the three isomeric dinitrobenzenes.



o-Dinitrobenzene — m-Dinitrobenzene

p-Dinitrobenzene — The Dinitrobenzene produced in this experiment

For this purpose 10 grams (or 8.3 cc.) of nitrobenzene are gradually added (under a hood) to a flask containing a mixture of 25 grams (or 14 cc.) of concentrated sulphuric acid and 15 grams (or 10.7 cc.) of fuming nitric acid. The mixture is heated for half an hour upon a water-bath, the flask being frequently shaken. This shaking is necessary on account of the immiscible character of the liquids and the more frequently it is thoroughly done the sooner the reaction is finished.

The following reaction has taken place:

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + HNO_3 = \underset{\text{m-Dinitrobenzene}}{C_6H_4(NO_2)_2} + H_2O$$

On cooling somewhat, the mixture is slowly poured into cold water which is constantly stirred. The insoluble yellow dinitrobenzene which turns solid is filtered off, washed with water, and pressed upon a porous plate or dried by pressing between thickly folded sheets of filter-paper.

When thoroughly dry it is recrystallized from alcohol.

Dinotrobenzene melts at 90°. The yield is 10–12 grams.

Experiment 4

Aniline from Nitrobenzene.

Fifty grams (or 42 cc.) of nitrobenzene and 90 grams of granulated tin are placed in a round-bottomed flask of 1½ liters capacity. To this mixture 200 grams (or 166 cc.) of hydrochloric acid are gradually added in the following manner: About one-tenth of the acid is added and an air condenser, a glass tube 3 feet long and ½ inch in diameter is attached to the flask in an upright position and the mixture well shaken. It becomes warm in a short time and ebullition begins. When this begins, the flask is immersed and rotated in cold water, or better, under water flowing from a faucet until the reaction has moderated.

The second tenth of the acid is then added and the above operation repeated. When one-half of the acid has been added, the violence of the action diminishes and the last half of the acid may be added in larger portions.

The reaction which takes place between the tin and acid is represented thus:

$$Sn + 2HCl = SnCl_2 + 2H$$

The nascent hydrogen from this reaction then reduces the nitrobenzene:

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H = 3H_2O + \underset{\text{Aniline}}{C_6H_5NH_2}$$

The aniline formed unites with the excess of hydrochloric acid present to form the hydrochloride:

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HCl = \underset{\text{Aniline hydrochloride}}{C_6H_5NH_2 \cdot HCl}$$

In order to make the reduction complete, the flask is heated for an hour on a water-bath. To separate the free aniline from the mixture, the warm solution is diluted with 100 cc. of water, then a solution of 150 grams of caustic soda in 200 grams of water is gradually added. The caustic soda sets the aniline free from its combination with hydrochloric acid and converts the stannous chloride into sodium stannate, from which the aniline is separated by a steam distillation.

If the liquid boils on adding a portion of the caustic soda, the flask should be cooled in water before adding more caustic soda. The action of the soda is:

$$C_6H_5NH_2 \cdot HCl + NaOH = C_6H_5NH_2 + NaCl + H_2O$$
$$SnCl_2 + 2NaOH = H_2SnO_2 + 2NaCl$$
$$H_2SnO_2 + 2NaOH = Na_2SnO_2 + 2H_2O$$
$$2Na_2SnO_2 + H_2O = Na_2SnO_3 + 2NaOH + Sn$$

After the entire solution has been added, the condenser is attached and steam is conducted through the resulting pasty liquid by means of a glass tube from a neighboring flask of water kept vigorously boiling. The tube should extend

almost to the bottom of the flask containing the mixture, inclined at an angle of 45° toward the flask of boiling water. The steam passes out of the flask into the condenser, through a tube ending just under the stopper, carrying with it the vapor of aniline and steam. The mixed aniline and water appears milky as it runs down the inner tube of the condenser.

Gradually the oily aniline collects under the water in the receiver. When the liquid appears no longer milky, the receiver is changed and some 250 cc. more liquid is distilled.

The distillates are now mixed, and 25 grams of common salt added for each 100 cc. of liquid, which is then shaken to dissolve all the salt. The aniline is extracted from the solution by shaking with ether in a separating funnel. The solution in ether is dried with a little solid caustic soda, and then (caution from *fire*) the ether is poured off into an evaporating dish and evaporated by placing it on a boiling water-bath under which the *light has been extinguished* before bringing the ether near it.

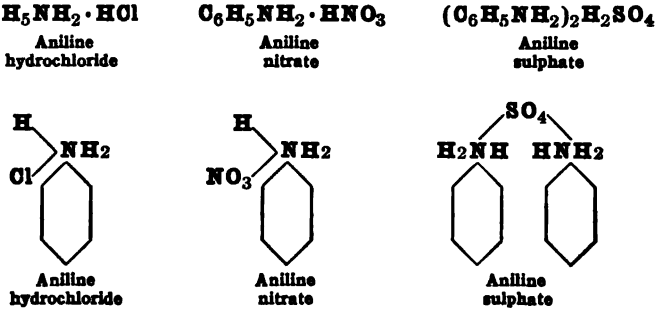
The aniline is then distilled. Its boiling-point is 182°. The theoretical yield may be very nearly attained.

Experiment 5

Formation of Aniline Salts. Into four watch-glasses, each about two inches in diameter, pour the following liquids in order and in amount enough to make them one-fourth full: First, water, second, dilute hydrochloric acid; third, dilute nitric acid; fourth, dilute sulphuric acid.

Add to each glass a single drop of aniline and note the effect. Use a separate clean glass rod to stir each liquid in turn and note what happens. Is there a difference in solubility of the aniline salts in the various acids and in the water?

FORMULAS OF THE ANILINE SALTS



EXPERIMENT 6

Solubility of the Aniline Salts in Aniline. Pour into each of the well-cleaned watch-glasses from the previous experiment enough aniline to make them one-fourth full. To the first add one drop of dilute hydrochloric acid; to the second one drop of nitric acid; to the third, one drop of sulphuric acid; and to the fourth, acetic acid in the same manner. Note the effect in each case. Stir the liquid carefully with a dry glass rod in each case. Does the aniline appear to dissolve the salts?

EXPERIMENT 7

Solvent Action of Aniline on Indigo. Drop a little finely powdered indigo into a few cubic centimeters of pure aniline contained in a test-tube. Warm the tube with shaking and examine the colors of the aniline by transmitted light, holding the tube nearly horizontal, and looking through it from below.

EXPERIMENT 8

A Blue Color from Aniline by Bleaching Powder. To a test-tube nearly full of water, add one drop of aniline and shake thoroughly. The aniline will dissolve. Pour out three-

quarters of the solution; add water to nearly fill the tube, and shake. To this dilute solution of aniline, add drop by drop a clear solution of bleaching powder in water.

A violet color will appear in the solution, growing darker with the successive additions of the bleaching-powder solution. This color changes quickly to brown.

Very dilute solutions give no color or a very faint one; but on addition of a few drops of a very dilute solution of ammonium hydrosulphide the liquid becomes rose colored. The limit of this reaction is one part of aniline in 250,000 parts of water. (Jacquemin, Ber., IX, 1433.)

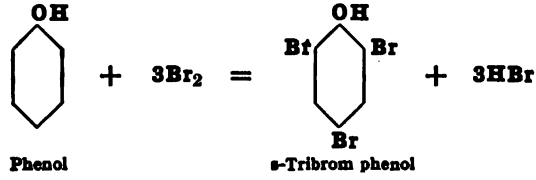
Experiment 9

Blue Color from Aniline by Acidulated Potassium Dichromate. To a test-tube containing about 1 cc. of concentrated sulphuric acid, add two drops of aniline. Carefully shake the tube and add an aqueous solution of potassium dichromate drop by drop with continual shaking until the liquid in the tube appears to turn black. Then pour a few drops of this liquid into a beaker of water standing on a sheet of white paper and stir it. The water will be colored a beautiful blue.

Experiment 10

A Violet Color from Phenol with Ferric Chloride. To a very dilute solution of phenol or carbolic acid, add a few drops of a solution of ferric chloride and note the effect. A violet color forms in the liquid.

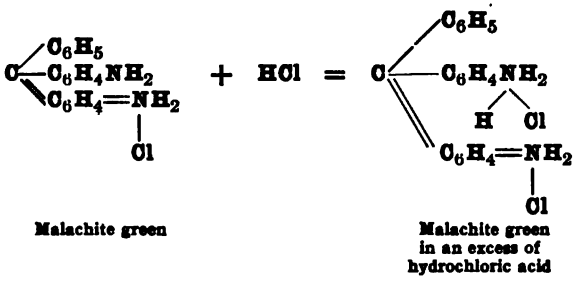
Add bromine water to a dilute solution of carbolic acid and notice the immediate turbidity caused by the tribromphenol formed.



Experiment 11

Action of Concentrated Hydrochloric Acid on Malachite Green. Make about 10 cc. of a concentrated solution of malachite green; then add concentrated hydrochloric acid until the color is turned to a reddish yellow. The dye has not been destroyed by the strong acid, but its color has been changed by the union of a molecule of the acid to a second amino group of the dye.

Into a glass cylinder of water held between the eye and a window, pour single drops of the above solution and note the gradual loss of the reddish-yellow color and the restoration of the original green, as the acid salt decomposes on its way down toward the bottom of the cylinder.



Experiment 12

Tannic Acid Lake of Malachite Green. Dissolve 5 grams of tannic acid and 5 grams of sodium acetate in 50 cc. of water. To a solution of 2 grams of malachite green in 200 grams of water, add the first solution with shaking as long as a precipitate keeps on forming. Allow it to stand several hours.

This insoluble precipitate is the tannic acid lake of the dye which is produced in the cotton fiber when it is mordanted with tannic acid and subsequently dyed in this color.

Experiment 13

Spirit-Soluble Malachite Green. Filter off the precipitate of the last experiment. Remove the filter from the funnel and spread it out in a warm place without disturbing the colored lake. When it is dry, separate it from the paper and pulverize a portion and dissolve it in alcohol. This spirit-soluble dye is used in coloring lacquers and varnishes.

Experiment 14

The Salting Out of a Dye. Prepare a solution of 1 gram of malachite green in 100 cc. of water. Sprinkle a few drops of the colored liquid on a piece of filter-paper. Now add to the remaining liquid 50 cc. of a saturated solution of common salt and shake thoroughly. Allow the liquid to stand quietly for a few minutes and notice what change has taken place. Sprinkle a few drops on filter-paper and compare the spots with those upon the first paper.

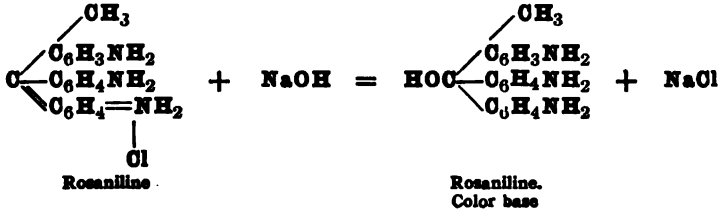
Experiment 15

Rosaniline Lake for Coloring Lacquers and Varnishes. To a solution of ½ gram of rosaniline in 100 cc. of water, add, in small portions as long as a precipitate forms, a solution containing 5 grams of tannic acid and 5 grams of sodium acetate in 50 cc. of water. Shake after each addition of tannic acid and allow the precipitate to settle before adding another portion.

Filter and wash the precipitate; then allow it to dry upon the filter in an air bath at 100° C. Pour alochol upon the dried precipitate and note that it dissolves. This insoluble tannate forms a spirit soluble dye for varnishes and lacquers.

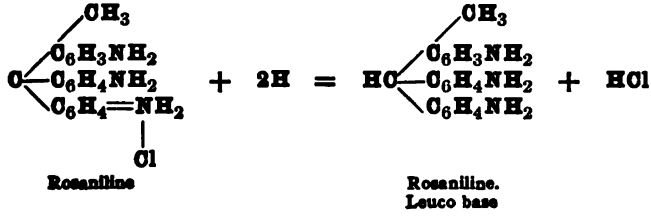
Experiment 16

The Color Base of Rosaniline. Add to a solution of ½ gram of rosaniline in water, a solution of sodium hydroxide in water until it is decolorized. The solution now contains the color base of rosaniline. Now add very dilute hydrochloric acid gradually and watch to see if the color returns. If the solution of rosaniline be sufficiently concentrated, the color base may be precipitated so that it can be seen on adding the sodium hydroxide.



Experiment 17

The Leuco Base of Rosaniline. To a solution fo rosaniline in a test-tube, add enough zinc dust to cover the bottom of the tube and then add hydrochloric acid drop by drop until the color disappears. This must be done very slowly and the addition of acid stopped just before the color has all disappeared. Place a drop of the solution on filter-paper and touch the spot with a drop of a solution of 1 gram of chromic acid in 100 cc. of water. The leuco base is formed by the reduction and the dye is reproduced by this oxidation.



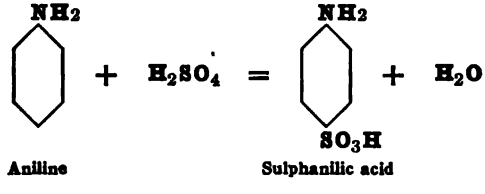
Experiment 18

Rosaniline Test Paper. An amount of rosaniline equal to a small bean is powdered and dissolved in 100 cc. in boiling water. The solution is then filtered and into it are dipped strips of filter-paper half an inch wide. They are dried by hanging them over a string in a place free from the slightest fumes of acid. These strips should not be red, but only a faint rose color. If the color is stronger, the solution should be diluted until the faint rose shade is reached.

Touch one of the dried strips with a drop of dilute acid. The spot turns white, due to the formation of a poly-acid salt of rosaniline. This paper is used to detect any excess of acid, e.g., in making aniline salts by gradually adding the acid to the aniline. Litmus-paper could not be used in this case; for litmus is turned even by the aniline salt itself. The rosaniline test-paper is not affected by the aniline salt. The amines in general are of such weakly basic character that the acid portions of their salts turn blue litmus red.

Experiment 19

Preparation of Sulphanilic Acid.



One hundred grams of concentrated sulphuric acid are poured into a dry flask, and then 30 grams of freshly distilled aniline are added in small portions with shaking. The mixture is then heated in an oil-bath to 180–190°, until on removing a few drops and adding caustic soda, no unchanged aniline separates.

To accomplish the compete conversion of the aniline will

require from four to five hours. The reaction mixture after cooling is poured into water that is constantly stirred. The sulphanilic acid separates out in crystals. It is filtered off and washed with water and recrystallized from boiling water. An addition of a little animal charcoal to the boiling solution will give a white product on filtering and allowing the acid to crystallize.

Experiment 20

Methyl Orange. Ten grams of sulphanilic acid, previously dried on the water-bath, are dissolved in 150 cc. of water containing 3.5 grams of anhydrous sodium carbonate. This solution is then treated with a solution of 4.2 grams of pure sodium nitrite in 20 cc. of water.

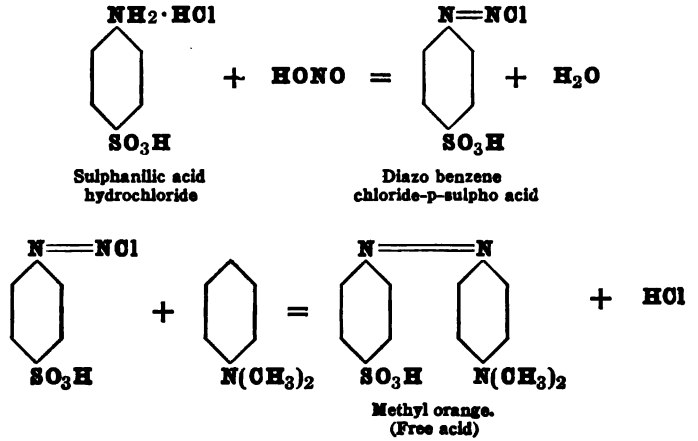
After cooling this mixture by immersing the beaker in cold water, hydrochloric acid is added to the extent of 2.5 grams of the anhydrous acid. To easily obtain this amount of acid, add to concentrated hydrochloric acid an equal volume of water. Find the specific gravity with the hydrometer. Consult a table for the amount of anhydrous acid in 1 cc., and take the number of cubic centimeters necessary to yield 2.5 grams of anhydrous acid.

Previous to diazotizing the sulphanilic acid, prepare a solution of 7 grams of dimethylaniline in the theoretical amount of hydrochloric acid. To neutralize the dimethylaniline, 25 cc. of water are added to it and then hydrochloric acid is added, a little with constant stirring. After each addition of acid a drop of the solution is placed on the rosaniline test paper to detect the slightest excess of free acid, which if present will decolorize the paper.

The solution of dimethylaniline thus obtained is added to the diazotized solution of sulphanilic acid and the mixture is made alkaline with a solution of caustic soda.

The methyl orange separates at once from the solution. The addition of 25 grams of finely powdered common salt and stirring until it is dissolved will cause the separation of more of the dye from the liquid.

The dyestuff is filtered and pressed out upon a porous plate or between thick folds of filter-paper. It is then recrystallized from a little water.



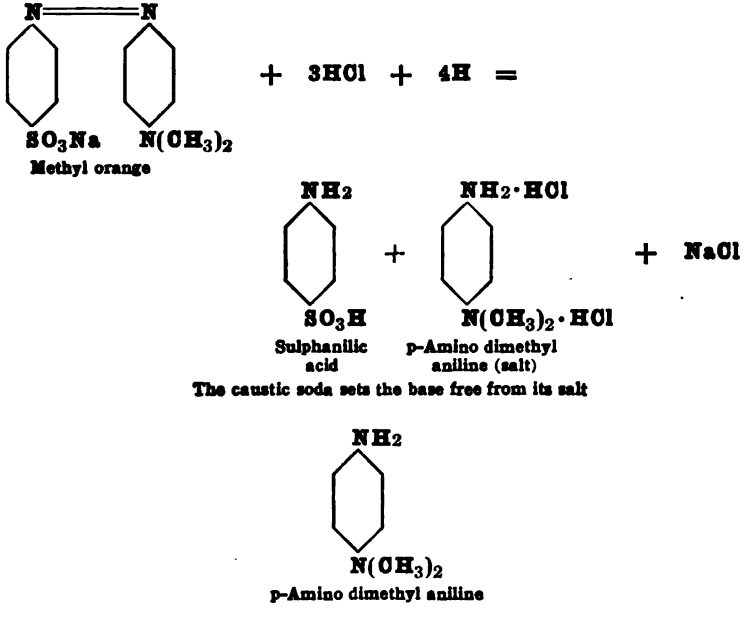
Experiment 21

Preparation of Para-aminodimethylaniline. Dissolve 2 grams of the dye, methyl orange, in as little boiling water as possible, and while the solution is kept hot on a water-bath, add gradually a solution of 8 grams of stannous chloride in 20 grams (17 cc.) of concentrated hydrochloric acid until the dye is decolorized. The solution is then cooled, and if the sides of the glass are rubbed with a glass rod, sulphanilic acid separates. It is then filtered through asbestos or glass wool. The filtrate is diluted with double its volume of water and a solution of caustic soda is added until the hydrate, which separates, is almost redissolved. The liquid will not become clear and the addition of the soda solution may be stopped when no further decrease of turbidity of the liquid is noticed.

It is then extracted several times with ether. The ethereal solution is dried with small pieces of solid caustic potash—allowing it to stand over night—the ether being finally poured

carefully off into an evaporating dish (*Caution:* Danger from fire) and evaporated as described in Experiment 4.

The para-aminodimethylaniline is left behind, having the appearance of an oil which, on rubbing with a glass rod, will solidify.



Experiment 22

Methylene Blue. Treat a portion of the para-aminodimethylaniline from the last experiment with small quantities of dilute sulphuric acid until it barely dissolves. This should be done with especial care not to use an excess of acid. A few drops of this solution are added to a *very* dilute solution of hydrogen sulphide in a beaker to which has been previously added $\frac{1}{60}$ of its volume of concentrated hydrochloric acid. Now add to this mixture a few drops of ferric chloride.

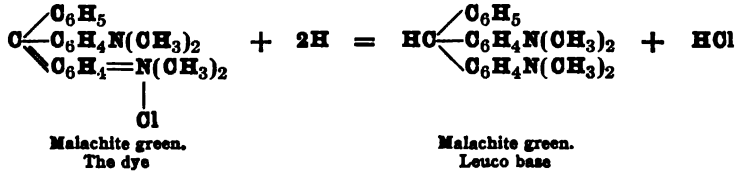
Methylene blue will be formed, giving an intense and beau-

tiful blue to the solution. This reaction, according to Emil Fischer, is a test for as small an amount of hydrogen sulphide as one part in 50,000,000 to 100,000,000 parts of water.

Experiment 23

Leuco Base of Malachite Green. To an aqueous solution of malachite green add zinc dust and then dilute hydrochloric acid very gradually, drop by drop, until the liquid is decolorized. Put a drop of the colorless liquid on filter-paper and touch the spot with a drop of a solution of one gram of chromic anhydride (CrO_3) in 100 cc. of water. The green color reappears.

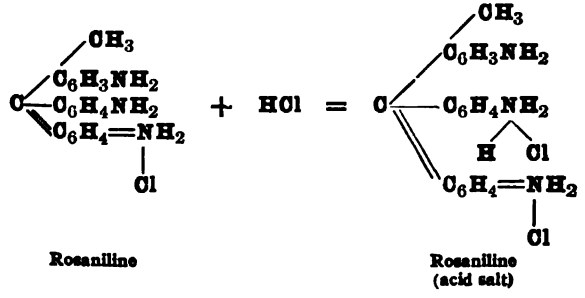
In this experiment the nascent hydrogen from the zinc and acid produces leuco-malachite green or diaminotriphenylmethane, according to the reaction:



On touching the spot on the filter-paper with chromic acid, oxidation takes place and malachite green is reformed.

Experiment 24

Action of Acids on Rosaniline.



To a concentrated aqueous solution of rosaniline in a test-tube, add concentrated hydrochloric acid, a few drops at a time, until the color turns reddish yellow. The solution now contains a certain hydrochloric acid salt of rosaniline which exists only in an acid solution.

Into a cylinder of water, held between the eye and the light, pour a few drops of this liquid and note the change to red as the drops fall farther and farther toward the bottom of the cylinder. The dilution soon becomes so great that the added molecule of hydrochloric acid is given up and the color of rosaniline returns.

Experiment 25

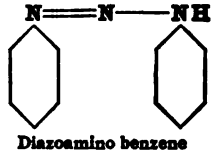
Preparation of Diazoaminobenzene.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HCl = \underset{\text{Aniline hydrochloride}}{C_6H_5NH_2 \cdot HCl}$$

$$C_6H_5NH_2 \cdot HCl + HONO = \underset{\text{Diazo benzene chloride}}{C_6H_5N{=}N{-}Cl} + 2H_2O$$

$$C_6H_5N{=}N{-}\boxed{Cl + H}\underset{\text{Aniline}}{HNC_6H_5} = C_6H_5N{=}N{-}HNC_6H_5 + HCl$$

Diazoamino benzene



Diazoamino benzene

Ten grams (or 9.6 cc.) of freshly distilled aniline are dissolved in a mixture of 100 cc. of water and 30.6 grams (or 25.5 cc.) of hydrochloric acid, sp.gr. 1.2. The solution is cooled by immersing the containing beaker in ice-water, and stirring. This solution is then diazotized by the addition of 8 grams of pure sodium nitrite in 50 cc. of water. A thermometer may be used as a stirring rod and the nitrite solution added slowly enough to keep the temperature below 10°.

A second solution of 10 grams of aniline in 50 grams of

water is previously prepared according to directions given above, employing exactly the theoretical amount of hydrochloric acid to unite with the aniline: the solution should not have enough free acid to decolorize rosaniline paper when a drop of the solution is placed upon it. This solution is well cooled with ice-water and then added to the diazo solution with constant stirring.

Then 50 grams of sodium acetate are dissolved in the least amount of water possible, well cooled, and added with stirring to the above mixture of the diazo compound acid and the aniline hydrochloride.

After standing for an hour, the diazoaminobenzene separates out and is filtered off with suction, washed several times with water and well pressed out between thick folds of filter-paper. It is recrystallized from ligroin.

The melting-point of diazoaminobenzene is 98°.

Experiment 26

Preparation of Aminoazobenzene. This experiment shows the molecular transformation of a diazoamino compound into an aminoazo compound.

Mix in a small beaker 10 grams of crystallized and finely pulverized diazoaminobenzene and 5 grams of pulverized aniline hydrochloride; then add 25 grams (or 24 cc.) of freshly distilled aniline. The mixture is now heated with constant stirring on the water-bath for an hour at 45°. At the end of the hour it is emptied completely into a larger beaker, water added, and dilute acetic acid until all the aniline has dissolved and the undissolved precipitate is wholly solid.

After filtering this off, it is washed with water and then heated in a large dish with about a liter of water and hydrochloric acid until most of the precipitate has been dissolved. Filter the solution and allow the filtrate to stand. Steel-blue crystals of aminoazobenzene separate after some time. These are filtered off and washed, *not* with water, but with dilute hydrochloric acid.

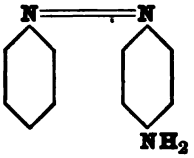
If the aniline hydrochloride required for this experiment is

not on hand, it may be prepared by adding aniline to hydrochloric acid while stirring and testing with rosaniline paper to avoid an excess of acid. After cooling, the pasty mass of crystals is filtered on asbestos or glass wool pressed firmly together on the filter by a pestle and spread out on a porous plate or folded filter-paper.

$$\underset{\text{Diazoaminobenzene}}{C_6H_5N{=}N{-}HNC_6H_5} + H\underset{\text{Aniline}}{C_6H_4NH_2} =$$

$$C_6H_5N{=}NC_6H_4NH_2 + C_6H_5NH_2$$

Aminoazobenzene



Aminoazobenzene

EXPERIMENT 27

Preparation of Benzene Monosulphonic Acid. To 150 grams of fuming sulphuric acid which contains 5–8 per cent of sulphuric anhydride (SO_3) in a 200-cc. flask, provided with an air condenser, add gradually with good shaking and cooling by water running over the outside of the flask, 40 grams (or 44.4 cc.) of benzene. Before adding the next portion, always wait until the last portion—which always floats on the surface of the acid—dissolves during the shaking. This process of sulphonation requires 10–15 minutes.

The resulting mixture is then added, with continual stirring, drop by drop, from a separating funnel, to three or four times its volume of a cold-saturated solution of common salt contained in a beaker. To prevent the beaker being heated above the room temperature the beaker is placed in a larger vessel filled with ice-water.

After some time and more quickly by rubbing the walls of the beaker with a sharp-edged glass rod, the sodium salt of

the benzene monosulphonic acid separates out in the form of leaflets with a greasy lustre. On long standing the quantity increases so much that the beaker may be inverted without spilling the contents.

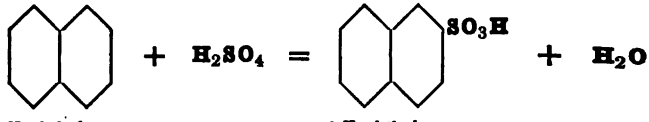
Should the separation of the crystals be long delayed, *10 cc.* of the liquid is poured into a test-tube, and cold water from the tap allowed to run over the outside of the tube while it is vigorously shaken and the inside of the tube rubbed with a sharp-edged glass rod. The solidified contents of the tube is poured back into the main quantity in the beaker. This hastens the crystallization of the whole. At times it may require several hours standing before the crystallization comes to an end.

The pasty mass of crystals is then filtered off with suction on a Buchner funnel, firmly pressed down with a mortar pestle and washed with a little saturated salt solution. The salt is dried by transferring it to a linen bag and squeezing it under a heavy pressure. It is then pulverized and heated to dusty dryness in an air bath at 110°. About 100 grams is the yield.

Dissolve 5 grams of this crude product in hot absolute alcohol; the adhering sodium chloride will not dissolve. Filter from this residue and, on cooling, the pure benzene monosulphonic acid will separate out.

Experiment 28

Preparation of β-Naphthalene Sulphonic Acid.



A mixture of 50 grams of pulverized naphthalene and 60 grams (or 33 cc.) of pure concentrated sulphuric acid are heated in an open flask in an oil bath for four hours at 170–180°.

When cool, the solution is carefully poured with stirring into one liter of water and the naphthalene which has not been attacked remains undissolved and is filtered off. If the filtration proceeds very slowly, the turbid liquid is poured off from the coarse pieces of naphthalene. The filtrate is neutralized at the boiling temperature in a large dish with a paste made by triturating 70 grams of dry slaked lime with warm water.

The resulting mixture is filtered as hot as possible through a wet filter cloth stretched over a frame. The precipitate is washed with hot water. The filter cloth is then folded together and thoroughly squeezed, letting the liquid run out into another dish. The resulting usually turbid liquid is filtered and united with the main portion.

This solution is evaporated in an open dish over a free flame until a test portion will solidify to a crystalline paste on rubbing with a glass rod. After allowing the solution to stand over night, the separated calcium β-naphthalene sulphonate is filtered off with suction. It is washed once with water and then pressed firmly together and spread out on folds of filter-paper.

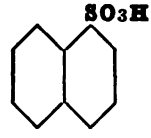
The sodium salt is obtained from this product by dissolving it in hot water and treating it gradually with a concentrated solution of 50 grams of crystallized sodium carbonate. After cooling the precipitated calcium carbonate is filtered off with suction, washed with water, and the filtrate evaporated over a free flame until crystals begin separating from the hot solution.

After standing several hours at the temperature of the room, the crystals are filtered off and the mother liquor further concentrated. Several hours later, the second lot of crystals is filtered off and these are united with the preceding lot and dried upon the water-bath. Yield, 60–70 grams.

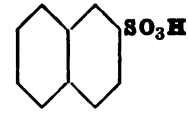
The naphthalene is sulphonated on heating with sulphuric acid, according to the following reaction:

$$C_{10}H_8 + H_2SO_4 = C_{10}H_7SO_3H + H_2O$$

In this experiment, however, there is formed not a single sulphonate, as in the case of benzene, but a mixture of two isomeric compounds whose formulas are:



α-Naphthalene sulphonic acid



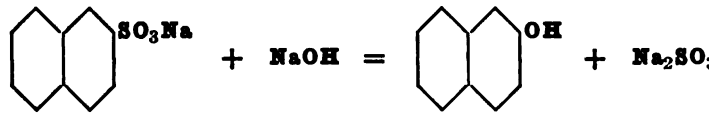
β-Naphthalene sulphonic acid

Which one of the two products shall be formed in the greater amount depends upon the temperature. At the temperature of the above experiment (170°) three parts of β-acid are formed to one part of α-acid.

If the experiment had been carried out at 100, then four parts of α-acid would have been formed to one part of β-acid. The separation of these acids depends upon the differing solubility of the calcium salts of the two isomeric acids. At 10° one part of α-salt dissolves in 16.5 parts of the β-salt and requires 76 parts of water for its solution. From a solution containing both salts, the more soluble β-salt must crystallize out first and thus by fractional crystallization be separated from its more soluble isomeric salt of the α-acid.

Experiment 29

Preparation of β-Naphthol from Sodium-β-Naphthalene Sulphonate.



Sodium-β-naphthalene sulphonate

β-Naphthol

10 parts sodium-β-naphthalene sulphonate;
30 parts sodium hydroxide (pure as possible);
1 part water.

The sodium hydroxide is broken into small pieces the size of a bean, treated with the water, and heated in a nickel crucible (11 cm. high and 8 cm. in diameter is a convenient size), with stirring at 280°.

The stirring is done with a thermometer the lower end of which is protected from the action of the fused caustic soda by a copper case or tube, about 16 cm. long and 8 mm. in diameter. The thermometer is supported by a one-hole stopper, having a canal cut down one side. The bottom of the tube is filled with oil to such a height as to cover the bulb of the thermometer. By pushing a perforated cork over the upper end of the thermometer case it may be used as the stirring rod. The hands should be protected by gloves and the eyes by glasses.

As soon as the melt reaches 280°, the heating is continued with a smaller flame and the sodium naphthalene sulphonate is added gradually with stirring. The temperature will fall after each addition; no more of the salt is added until the temperature again rises to 280°.

When all the salt has been added, the flame is increased somewhat and then the mass becomes pasty with evolution of steam and frothing, and finally, at about 310°, the real reaction takes place. By holding the temperature at 310–320° for about five minutes the mass liquefies and the reaction is complete. The melted mass is poured upon a strong copper plate with upturned edges, of such a size that the plate is covered with only a thin layer of the liquid. The portions of the dark sodium naphtholate may be easily distinguished from the brighter caustic soda. When the mass is cold, it is broken up and dissolved in water. The naphthol itself is precipitated at the boiling temperature by the addition of concentrated hydrochloric acid (under the hood), and after cooling extracted with ether.

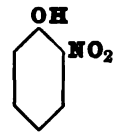
The ethereal solution is dried over fused anhydrous Glauber's salt and the ether distilled off and saved; a fractionating flask with a wide delivery tube is used. When the ether has been removed, the naphthol remaining behind is distilled over without using a condenser.

Melting-point of β-naphthol is 123°; the boiling-point, 286°. Yield, half the weight of the sulphonate used.

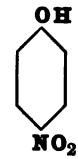
Experiment 30

Preparation of o- and p-Nitrophenol.

$$C_6H_5OH + HNO_3 = C_6H_4(OH)NO_2 + H_2O$$



o-Nitrophenol



p-Nitrophenol

In 200 cc. of hot water are dissolved 80 grams of sodium nitrate; the solution is then cooled and treated while being stirred with 100 grams of concentrated sulphuric acid. When the mixture has been cooled to 25°, add from a drop funnel, drop by drop, with constant stirring, a mixture of 50 grams of crystallized phenol and 5 grams of alcohol, which has been melted by gentle warming. During this time the temperature is kept between 25–30° by immersing the containing beaker in water. Should the phenol mixture solidify in the drop funnel, it may safely be melted again by pouring warm water over the outside of the drop funnel and then wiping it dry.

When the reaction mixture has stood for two hours, it is treated with frequent stirring, with double its volume of water; the desired product separates and collects as an oil at the bottom of the beaker. The chief portion of the water is then poured off from the oil; this residue is washed with water and after adding ½ liter of water it is distilled with steam until no more *o*-nitrophenol passes over. Should the nitrophenol solidify in the condenser, it may be removed by withdrawing the water from the condenser and then as the temperature rises from the passage of the steam it will melt

and flow out. On readmitting the cold water, it must be done slowly to prevent cracking the hot glass tube.

The distillate is cooled and filtered. The separated *o*-nitrophenol is washed with water and pressed out on a porous plate or between thick folds of filter-paper and dried in a desiccator. It is then obtained quite pure.

The non-volatile *p*-nitrophenol has remained during the above distillation in the flask. In order to obtain it, the mixture is cooled by immersion in cold water. The aqueous solution is then filtered off from the insoluble portion; the filtrate is then boiled for 15 minutes with 20 grams of animal charcoal; the water which evaporates is replaced by an equal quantity. The charcoal is filtered off, and the filtrate allowed to stand in a cool place over night and the *p*-nitrophenol separates out in long, nearly colorless crystals (needle-shaped). Any oil still remaining in the distillation flask is boiled with a mixture of one part of concentrated hydrochloric with the use of animal charcoal.

o-Nitrophenol melts at 45°; yield, 30 grams.

p-Nitrophenol melts at 114°; yield, 5–10 grams.

Experiment 31

The Preparation of Malachite Green. 1. *The Preparation of the Leuco Base.* A mixture of 50 grams of dimethylaniline and 20 grams of benzaldehyde is heated in a porcelain dish frequently stirred, on a water-bath for four hours, with 20 grams of zinc chloride which has been previously prepared for this purpose by fusion in a porcelain dish and pulverization when cold.

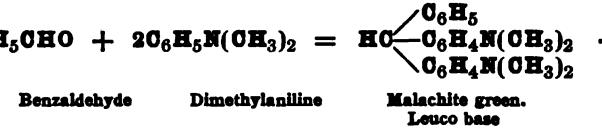
The product is a viscous mass which cannot be poured directly from the dish. To melt it, boiling water is poured upon it while it is being heated on a water-bath. While still hot, it is poured into a half-liter flask.

Steam is passed into it until no more drops of dimethylaniline appear in the attached condenser. The product remains behind in the flask as a non-volatile sticky mass which adheres firmly to the walls. This is the impure leuco

base of the dye. When the contents of the flask have become cold, the aqueous portion is poured off; the base, sticking to the walls of the flask, is washed several times with water and then dissolved in the flask with alcohol while it is being warmed on the water-bath.

The alcoholic solution is filtered and allowed to stand over night in a cool place. The pure base separates out in colorless crystals. These are filtered off and washed with alcohol and dried by pressing between the folds of filter-paper and subsequent exposure to the air. A second product may be obtained by evaporating the mother liquor to one-half its volume and allowing it to stand in a cool place.

Should the base separate from its alcoholic solution as an oil instead of in the form of crystals, this is due to the use of an insufficient quantity of alcohol for the solution. To remedy this more alcohol is added and the mixture is heated until the oil has dissolved and the cooling is repeated.



2. *Oxidation of the Leuco Base and Its Conversion into Malachite Green.* Dissolve 10 grams of the leuco base (thoroughly dried) by heating it in a quantity of dilute hydrochloric acid, which corresponds to 2.7 grams of anhydrous acid. To obtain this amount of acid, dilute pure hydrochloric acid with double its volume of water, determine its specific gravity, and by reference to a table find how much anhydrous acid the solution contains. Calculate how many cubic centimeters of this solution must be taken to get the required 2.7 grams of anhydrous acid.

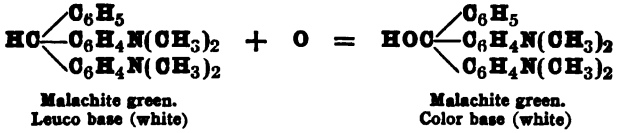
The colorless solution of the leuco base in this amount of acid is then diluted in a large beaker with 800 cc. of water and treated with 10 cc. of 40 per cent acetic acid (sp.gr.1.0523), prepared by gradually diluting glacial acetic acid with water.

The mixture is well cooled by adding pieces of ice; then with stirring gradually add, during five minutes, a quantity of lead peroxide paste which contains 7.5 grams of pure lead peroxide. The peroxide is weighed off in a beaker and stirred with the addition of sufficient water to make a very thin paste.

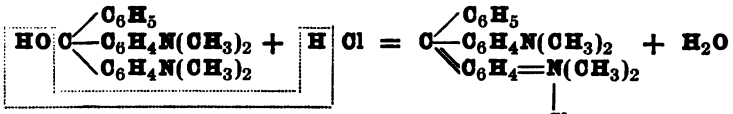
After adding the peroxide, the mixture is allowed to stand five minutes with frequent stirring; then add a solution of 10 grams of Glauber's salt, dissolved in 50 cc. of water. The solution, after stirring and allowing to stand for five minutes, is filtered through a folded filter from the precipitate of lead sulphate and lead chloride. The filtrate is treated with a filtered solution of 8 grams of zinc chloride, dissolved in the least possible amount of water; a saturated solution of salt is then added until the dye is wholly precipitated.

The complete precipitation of the dye may be easily recognized by bringing a drop of the solution with a glass rod on a filter-paper when a bluish green precipitate will appear, surrounded by a circle of still fainter light-green color.

The precipitated dye is now filtered off with suction, washed with a little saturated salt solution, and pressed out between folds of filter-paper. To further purify it, the dye may be dissolved again in hot water, and after filtering and cooling, thrown out by adding the saturated salt solution.



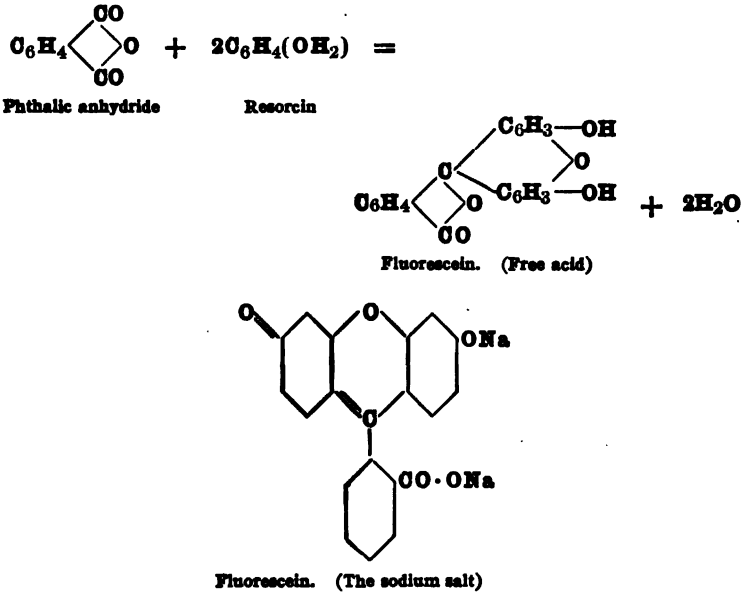
Malachite green. Leuco base (white) — Malachite green. Color base (white)



The dye: Malachite green

EXPERIMENT 32

The Preparation of Fluorescein.



Thoroughly mix and grind together in a mortar 15 grams of phthalic anhydride and 22 grams of resorcin and heat the mixture in a small beaker suspended in an oil bath to 180°. To the mass when fused, add while stirring, and in the course of ten minutes, 7 grams of pulverized zinc chloride. This is easily prepared as follows: Ten grams of the commercial salt, which always contains water, are carefully heated in a porcelain dish over a free flame until it melts. When it has been kept in a fused condition for a few minutes it is cooled and the solidified substance is removed from the dish and pulverized. (The commercial salt referred to is the anhydrous and not the crystallized zinc chloride.)

After the addition of the 7 grams of the anhydrous salt, the temperature is increased to 210° and the heating con-

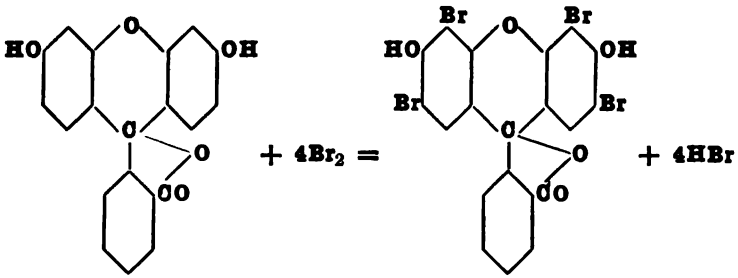
tinued until the liquid, which gradually thickens, becomes solid, for which one-half hour may be necessary.

The cold brittle product is removed from the beaker by gently chipping at the edge of the solid cake with a sharp knife and then cracking out the cake in fragments, or it may be more quickly done by breaking the beaker and removing the pieces of glass adhering to the cake. The product is finely pulverized and boiled ten minutes in an open dish with 200 cc. of water and 10 cc. of concentrated hydrochloric acid. This effects the solution of the substance which did not enter the reaction; the hydrochloric acid is necessary to dissolve the zinc oxide and basic chloride. The fluorescein is filtered from the solution, washed with water until the filtrate is no longer acid and then dried on the water-bath.

The insoluble fluorescein is easily soluble in a solution of caustic soda. To a little of the powder, enough to cover the bottom of a test-tube, add, drop by drop, with shaking, a solution of caustic soda until the fluorescein dissolves. Pour the solution into a large cylinder of water drop by drop. As the heavy solution sinks down into the water a splendid green fluorescence will be noticed by reflected light, especially if the observer walks around the vessel during the experiment.

Experiment 33

The Preparation of Eosine.

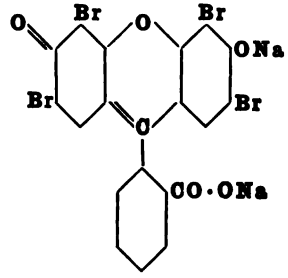


Fluorescein. (Free acid)

Eosine. (Tetra-brom-fluorescein) free acid

Place 15 grams of fluorescein in a flask and pour upon it 75 cc. of alcohol (about 95 per cent), and add with frequent shaking 33 grams of bromine, drop by drop, from a Winckler's burette. This prevents any danger from the bromine coming in contact with the fingers. As the specific gravity of bromine is very nearly 3, the 33 grams will occupy 11 cc.

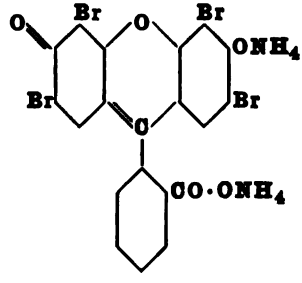
As the bromine is being added, it will be noticed that the the portion of the fluorescein which has not dissolved in the alcohol steadily diminishes and that as soon as about one-half the bromine has been added, a clear dark reddish-brown solution is formed. This is due to the fact that the fluoerscein dibromide, which is first formed, is easily soluble in alcohol. By the further addition of bromine, the fluorescein tetrabromide or eosine is produced. This, since it is only slightly soluble in alcohol, separates out in the form of brick-red leaflets. When all the bromine has been added, the mixture is allowed to stand for two hours, the precipitate is then filtered off, washed several times with alcohol, and dried upon the water-bath. The product so obtained is a compound of one molecule of eosine and one molecule of alcohol. Pure eosine is obtained from it by heating in an air bath at 110°. During the heating the color brightens. Since eosine is itself insoluble in water, the soluble salt of sodium, potassium, or ammonium is prepared for use as the dye.



Sodium salt, eosine

EXPERIMENT 34

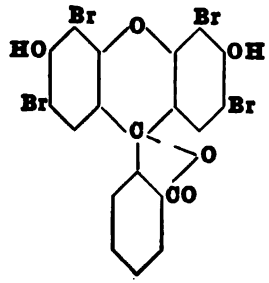
The Salts of Eosine.



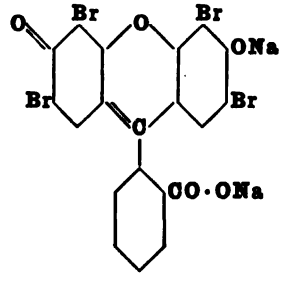
Ammonium, eosine

1. *Ammonium Eosine.* Pour into a crystallizing dish sufficient concentrated ammonia to fill it one-eighth full. Over the top of the dish place a strong filter-paper large enough to allow the edge to be pressed carefully down over the rim of the dish and tied firmly. Upon the paper the acid eosine is now spread in a layer about ½ cm. in thickness and the whole covered with a glass funnel. The ammonia gas ascending through the brick-red powder of the free acid makes it gradually assume the darker color of the ammonium salt. In about three hours the conversion is complete and the product consists of dark red crystals of a greenish lustre. The end of the reaction is determined by adding a little of the powder to water. If it dissolves the reaction is ended.

2. *Sodium Eosine.* Grind 6 grams of eosine with 1 gram of anhydrous sodium carbonate and place it in a beaker not too small. Moisten the powder with alcohol and add 5 c.c. of water. Heat it upon the water-bath until no more carbon dioxide is evolved. To the resulting aqueous solution of sodium eosine, add 20 grams (or 25 cc.) of alcohol, heat to boiling, and filter the solution. When it is cold, the sodium salt separates out in the form of splendid red needles with a metallic lustre. As in the case of many dyes, the crystallization requires a long time—a day at least is necessary.



+ 2NaOH =

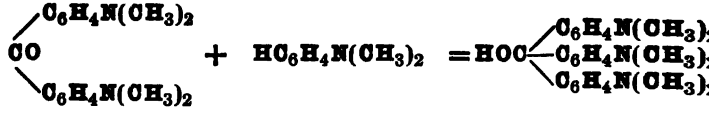


+ $2H_2O$

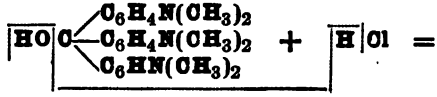
Sodium eosine

Experiment 35

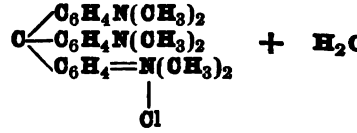
Preparation of Crystal Violet.



Michler's ketone | Dimethyl aniline | Crystal violet. Color base



Crystal violet. Color base



Crystal violet. The dye

A mixture of 25 grams of dimethylaniline, 10 grams of Michler's ketone, and 10 grams of phosphorus oxychloride is heated in an open dry flask for five hours on an actively boiling water-bath. The blue-colored product is then poured into water, made alkaline with a solution of caustic soda and subjected to a steam distillation until no more drops of unattacked dimethylaniline pass over. When cool, the solidified color base remaining in the flask is filtered off from the alkaline solution, washed with water, and then boiled with a mixture of 1 liter of water and 4.2 cc. of concentrated hydrochloric acid. The blue solution that is formed is filtered while hot from the color base which remains undissolved and to be saved. This latter is again boiled with a fresh quantity of dilute hydrochloric acid; this operation is repeated until the residue is almost entirely dissolved. The blue solutions thus obtained are united and when cold, pulverized salt is added with constant stirring until the dye is precipitated.

It is then filtered with suction and pressed out between folds of filter-paper and crystallized from a little water.

During cooling, the crystal violet forms coarse crystals of a greenish lustre; these are filtered off and dried in the air upon filter-paper.

Experiment 36

Preparation of Auramine O. In a mortar, 25 grams of Michler's ketone are thoroughly mixed with 25 grams of ammonium chloride and 25 grams of anhydrous zinc chloride (commercial *anhydrous* zinc chloride is melted in a porcelain dish and kept in a state of fusion for ten minutes, then cooled, and pulverized).

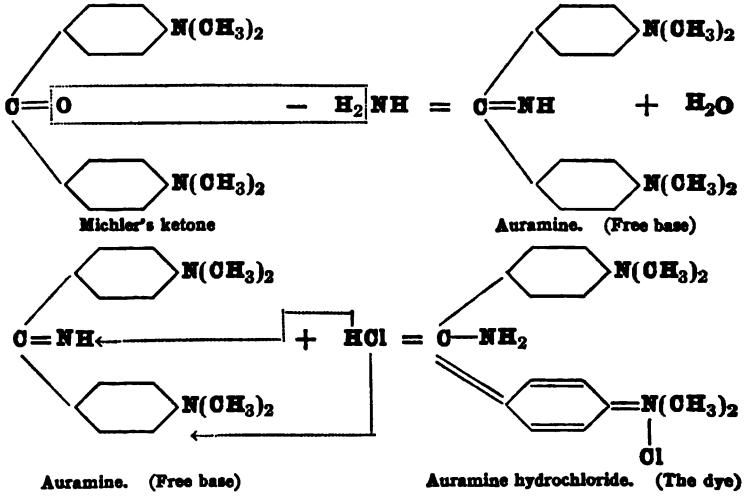
The mixture is now transferred into a porcelain jar or a glass beaker, which is then suspended in an oil bath. The temperature of the bath is raised to 200°. The mixture gradually melts and turns yellow.

From time to time the mass is well stirred, and the fused mass is kept at a temperature of 150–160° for four or five hours. The end of the reaction may be recognized by making

a test in hot water of a small portion, which should almost completely dissolve.

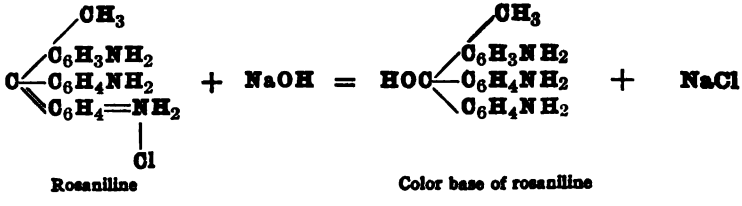
After cooling, the melt is removed with a little chisel, finely powdered, and treated with cold water containing a little hydrochloric acid in order to dissolve the excess of ammonium chloride and the zinc chloride. The residue is then extracted with water at 60–70° (higher temperature causes hydrolysis), filtered from any unchanged ketone, and salt added to the filtrate with stirring until the dye separates out. It is then filtered off and dried between folds of filter-paper.

The crystalline product is purified by recrystallization from hot water, which should not be above 70°. The product is a powder of a sulphur-yellow color.



EXPERIMENT 37

Preparation of Rosaniline Color Base.

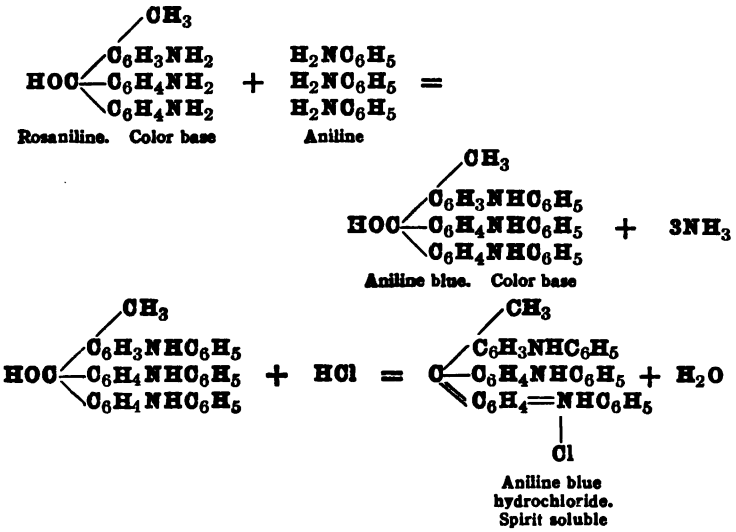


In one liter of boiling water, 15 grams of powdered rosaniline are dissolved with stirring. When assured that solution is complete, add gradually with constant stirring a concentrated solution of caustic soda until the red liquid is decolorized. The rosaniline base appears as an insoluble colorless or pinkish amorphous precipitate. This is filtered off, washed with water, and pressed out until dry between the folds of filter-paper. Expose a little of this powder to the air upon a slightly moistened filter-paper, and by the action of the carbonic acid of the air it will turn red.

Place in a test-tube enough of the rosaniline base to cover the bottom of it, add 20 cc. of water and shake; the insoluble base is simply suspended in water. Now add very gradually, with constant shaking, dilute hydrochloric acid. The base reacts to form a salt which dissolves, giving the characteristic rosaniline color to the solution.

Experiment 38

Spirit-Soluble Aniline Blue or Opal Blue.



Ten grams of rosaniline base (from Exp. 37), 100 grams of aniline, and 1.2 grams of benzoic acid are placed in a flask provided with a thermometer and a bent tube to conduct away a little aniline, ammonia, and water, which distil off during the process. The flask is placed upon a sand bath and heated gradually to 180°. It is kept at this temperature until a few drops of the hot liquid dissolved in alcohol and a little glacial acetic acid, when poured upon a filter-paper, show a pure blue by daylight which is tinged only slightly red by gaslight. The heating requires about three hours.

The hot melted product is then poured into a beaker, and when cooled a little 100 cc. of pure concentrated hydrochloric acid (28 per cent) are gradually added with stirring. The aniline blue is thus precipitated, while an impure blue remains dissolved in the mixture of aniline and aniline hydrochloride (formed by the neutralization of a part of the aniline). The mixture, filtered hot at the pump, is washed with boiling water to which a few drops of hydrochloric acid have been added. The aniline blue thus obtained is dried on the water-bath. It appears in the form of a greenish or reddish-brown crystalline powder. The yield is about 12 grams.

The filtrate contains an impure blue. This is obtained by acidifying with hydrochloric acid until no further precipitation occurs. The precipitate is filtered off, washed, and dried as above. About 6 grams of the impure blue are obtained. It dyes duller shades than the opal blue.

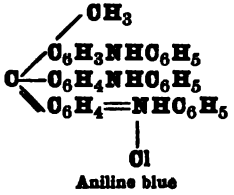
The shade and the yield obtained depend largely upon the time of heating. The temperature must not be allowed to exceed 180°.

Experiment 39

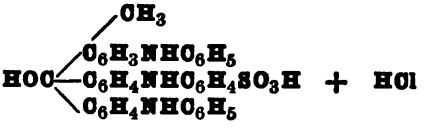
Preparation of Alkali Blue. In a 200-cc. flask are placed 56 cc. of concentrated sulphuric acid. Ten grams of aniline blue in the form of a fine crystalline powder are slowly added, so as to keep the temperature below 35°. The apparatus should be placed under a hood, as fumes of hydrochloric acid are evolved.

When all the aniline blue is dissolved, the temperature is kept at 35–40°, until a few drops diluted with water and filtered yield a residue which dissolves in a weak boiling solution of caustic soda. As soon as this condition has been attained, the sulphonation mixture is poured into 800 cc. of cold water, filtered at the pump, and the precipitate washed with water until free of acid.

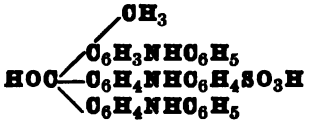
The moist free acid of the dyestuff is then transferred to a porcelain evaporating dish and hot water added to make a thin paste. The sodium salt is then formed by cautiously adding a solution of caustic soda, the whole being raised to boiling. If the right amount of soda has been added, a sample will dissolve without a residue in hot water with a blue color. An excess of alkali produces a brown color, and if this is the case, dilute sulphuric acid is slowly added with stirring until the right color is regained. The solution is evaporated not quite to dryness, and finally dried completely at about 50°.

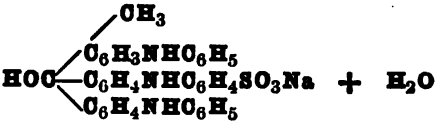


Aniline blue



Alkali blue. (Free acid)



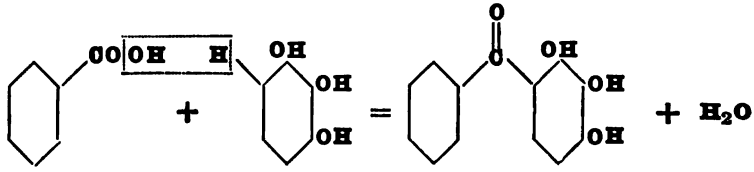


Alkali blue

Experiment 40

Alizarine Yellow A. A thorough mixture of 12 grams of pyrogallic acid, 12 grams of benzoic acid, and 36 grams of pulverized anhydrous zinc chloride is made by grinding them together in a mortar. The mixture is placed in a 200-cc. porcelain jar or glass beaker and immersed in an oil bath. The temperature is slowly raised to 145° and the reaction is finished when no more foaming occurs and the brown color does not increase.

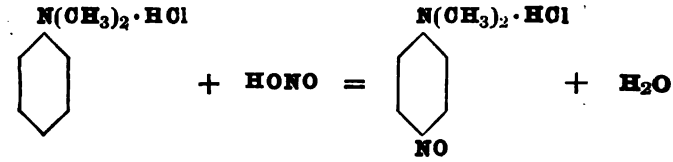
When it is cold, the product is pulverized and boiled with water and a little animal charcoal and filtered. The needle-shaped crystals of the dyestuff separate on cooling and they are filtered off and dried.



Benzoic acid — Pyrogallic acid — Alizarine yellow A.

Experiment 41

Nitroso Dimethyl Aniline Hydrochloride.



Dimethyl aniline hydrochloride — Nitroso dimethyl aniline hydrochloride

A 200-cc. beaker is charged with 69 cc. of concentrated hydrochloric acid, and into this is slowly poured, with stirring, 20 grams of dimethyl aniline. Ice is then added until the temperature has fallen to 0°. In a small quantity of water, 12 grams of sodium nitrite are dissolved and this solution is

slowly added to the solution of dimethyl aniline hydrochloride, which is stirred mechanically. The temperature should be kept at 8°, or under, by adding pieces of ice from time to time.

The hydrochloride of nitroso dimethyl aniline separates and after standing for some time it is filtered from the suction pump, washed with a little dilute hydrochloric acid, and dried between folds of filter-paper.

Experiment 42

Preparation of Methylene Blue. Twelve grams of dimethyl aniline are dissolved in a mixture of 40 cc. of water and 65 cc. of concentrated hydrochloric acid. Pieces of ice are added with stirring until the temperature falls to 12–15°. While this solution is being stirred mechanically, a solution of 7.1 grams of sodium nitrite is run slowly through a glass tube which dips *under* the surface of the liquid. Pieces of ice are added as needed to prevent the temperature rising above 15°.

The nitroso dimethyl aniline thus formed is reduced by the careful addition of 20 grams of zinc dust. The reduction is complete when the solution attains a clear red color. The amount of zinc added must be sufficient to completely neutralize the hydrochloric acid, so that a piece of Congo-red paper is no longer turned blue.

A sufficient quantity of water is now added to dilute the solution to 500 cc.; then a solution of 12 grams of dimethyl aniline in the exact amount of hydrochloric acid to form the hydrochloride is added, and, further, a solution of 50 grams of sodium thiosulphate in a little water.

This product is then oxidized by the addition of 25 grams of potassium dichromate and boiling for two hours. Thirty cc. of concentrated sulphuric acid diluted with 100 cc. of water (avoid accident by pouring the acid into the water with constant stirring) are now added and the solution is boiled to expel the evolved SO_2.

The resulting leucomethylene blue is oxidized by the addition of 8 grams of neutral sodium chromate in a little water.

The dye is precipitated by the addition of salt, until on stirring no more will dissolve.

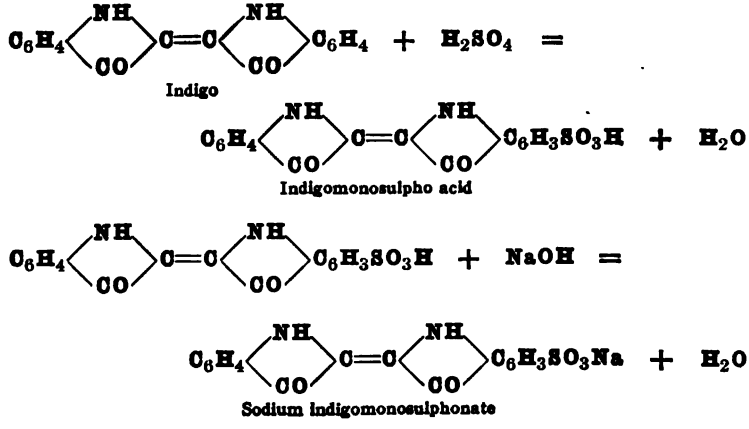
The base so produced is filtered off and dissolved in a little boiling water to which a small amount of hydrochloric acid has been added, and the hydrochloride formed is precipitated out by common salt, filtered and dried between folds of filter-paper.

Experiment 43

Indigomonosulpho Acid. Pulverize 5 grams of indigo as finely as possible and treat it with 20 grams of concentrated sulphuric acid in a porcelain dish for not more than half an hour, stirring well from time to time. Pour the resulting product into a half liter of water. Stir the liquid thoroughly and allow to settle for an hour.

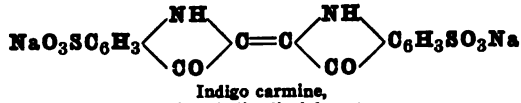
Carefully pour off the blue liquid through a filter so as not to disturb the residue. Transfer this residue to the filter and wash twice with water. Wash out the solid substance from the filter into a beaker; add 100 cc. of water and then slowly add a solution of caustic soda until the liquid is alkaline.

Filter from any unchanged indigo and evaporate the solution on the water-bath. The dry product is a sodium salt of indigomonosulpho acid, often called indigo purple, red extract of indigo, and red indigo carmine, mixed with sodium sulphate.



EXPERIMENT 44

Indigodisulpho Acid. Sulphindigotic Acid. Five grams of finely pulverized indigo are mixed thoroughly with 60 grams (or 33.3 cc.) of strong sulphuric acid and heated to 90° for half an hour. Pour the resulting pasty mass slowly with constant stirring into 300 cc. of water. Any unchanged indigo is removed by filtering and at the same time any insoluble indigomonosulpho acid. The blue filtrate contains the indigodisu pho acid. By adding to this a saturated solution of common salt, the sodium salt of the acid is precipitated. The precipitate is collected upon a filter and washed with a saturated solution of salt. It is dried by pressing on a porous plate or between folds of filter-paper. The product is indigo carmine:



Indigo carmine,
Sodium indigodisulphonate

EXPERIMENT 45

Dioxytartaric Acid

$CO_2HC(OH)_2 \cdot C(OH)_2CO_2H$ or $CO_2H \cdot CO \cdot CO \cdot CO_2H$

Forty grams of tartaric are gently warmed with 80 grams of fuming nitric acid until dissolved. An equal volume of concentrated sulphuric acid is slowly added with stirring and the whole is allowed to stand over night.

The resulting crystalline magma is then stirred into ice and water, and the solution is left to stand three or four days, after which it is neutralized with sodium carbonate. The nearly insoluble sodium dioxytartrate which separates is filtered off, washed and dried.

Phenylhydrazin-p-sulphonic Acid. Forty grams sodium salt of sulphanilic acid are diazotized in the usual way by employing 48 grams hydrochloric acid and 12 grams of sodium nitrite. The well-cooled solution is poured into a solution of 50.4 grams of pure sodium bisulphite. The liquid becomes

reddish yellow, red, and then yellow again. It is allowed to stand over night. Hydrochloric and zinc are gradually added with stirring until the solution is completely decolorized, after which it is boiled, filtered and evaporated to the point of crystallization. Yield 85 per cent.

Tartrazine. Ten parts of sodium dioxytartrate are stirred into 16 parts of water and warmed to 40° C. when the required amount of hydrochloric acid (13 parts) is added. The solution is filtered and added to a clear solution of 20 parts of phenylhydrazine-p-sulphonic acid dissolved in 60 parts of water containing 10 parts of 30 per cent solution of sodium hydroxide. The mixed solutions are warmed to 80° C. and allowed to cool when the precipitate of tartrazine is filtered off, pressed, and dried.

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The capital letters in parentheses attached to many names of dyes stand for the names of firms manufacturing them, the meaning of which is shown in the following list:

A	Actiengesellschaft für Anilinfabrikation, Berlin.
B	Badische Anilin- und Sodafabrik, Ludwigshafen.
By	Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld a. Rhein.
BK	Leipziger Anilinfabrik Beyer & Kegel, Lindenau-Leipzig.
C	Leopold Casella & Co., Frankfurt a. M.
D	Dahl & Co., Barmen.
DH	L. Durand, Huguenin & Co., Basle and Hüningen.
H	Read Holliday & Sons, Limited, Huddersfield.
I	Société pour l'Industrie Chimique, Basle.
K	Kalle & Co., Biebrich a. Rhein.
L	Farbwerk Mülheim (formerly A. Leonhard).
Lev.	Levinstein, Crumpsall Vale, Manchester.
M	Farbwerke vorm. Meister Lucius & Brüning, Höchst a. M.
Mo.	Société Chimique des Usines du Rhône (formerly Gilliard, Mounet & Cartier).

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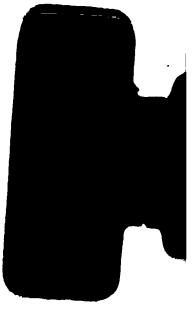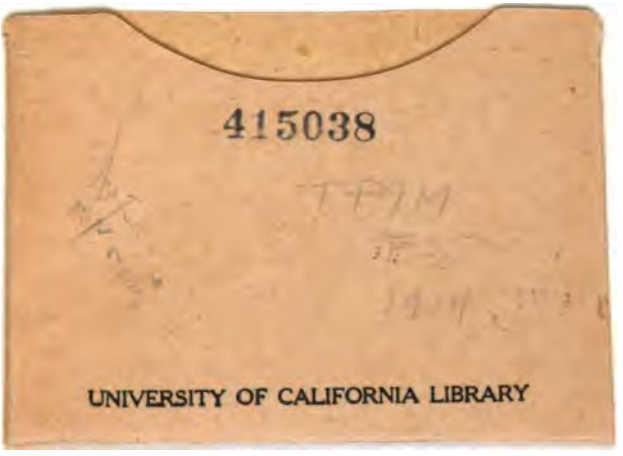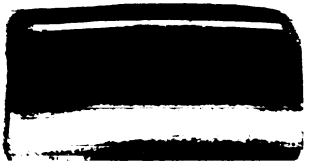
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